

# COLLEGE CHEMISTRY

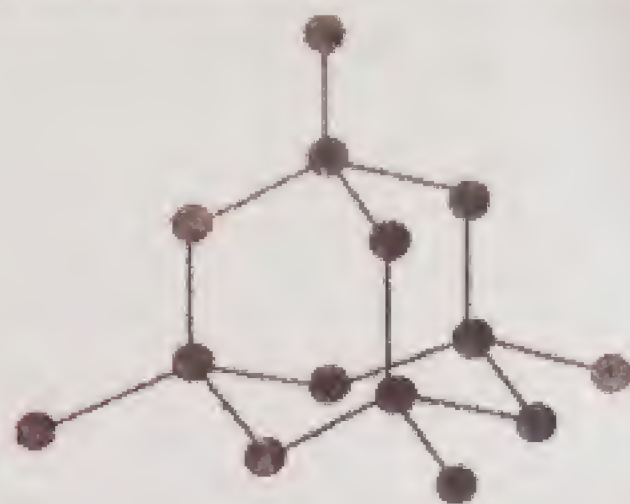
For Intermediate Part II

Shahid Ali  
Prof. M. Nadeem  
Sarwat Tahir



Education  
Tahir





# CHAPTER # 13

## s and p-BLOCK ELEMENTS

### PERIOD 3 (Na to Ar)

### ATOMIC AND PHYSICAL PROPERTIES OF THE PERIOD 3 ELEMENTS

This period contains Sodium (Na), Magnesium (Mg), Aluminum (Al), Silicon (Si), Phosphorus (P), Sulphur (S), Chlorine (Cl) and Argon (Ar).

#### (A) ATOMIC PROPERTIES

##### (1) ELECTRONIC STRUCTURES

In Period 3 of the Periodic Table, the valence orbitals are 3s and 3p orbitals. They are filled with electrons. The short electronic structures are:

<sup>11</sup> Na	[Ne] 3s <sup>1</sup>
<sup>12</sup> Mg	[Ne] 3s <sup>2</sup>
<sup>13</sup> Al	[Ne] 3s <sup>2</sup> 3p <sup>1</sup>
<sup>14</sup> Si	[Ne] 3s <sup>2</sup> 3p <sup>2</sup>
<sup>15</sup> P	[Ne] 3s <sup>2</sup> 3p <sup>3</sup>
<sup>16</sup> S	[Ne] 3s <sup>2</sup> 3p <sup>4</sup>
<sup>17</sup> Cl	[Ne] 3s <sup>2</sup> 3p <sup>5</sup>
<sup>18</sup> Ar	[Ne] 3s <sup>2</sup> 3p <sup>6</sup>

In each case, [Ne] represents the complete electronic structure of a neon atom. (i.e. 10 electrons)

#### QUICK QUIZ-1

(1) The electron structure of Mg is 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>. Write down electron structure of Al in the same notation.

<sup>13</sup>Al 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>, 3p<sup>1</sup>

(2) Which of the two elements Mg or Al has the more stable structure?

Mg has more stable structure. It is because it has completely filled 3s-valence orbital (i.e. 3s<sup>2</sup>). On the other hand Al has one valence electron in 3p-orbital which can be easily removed. Hence, Mg has more stable electronic structure. This is also indicated by high first ionization energy of Mg than that of Al.

##### (2) TRENDS IN ATOMIC RADIUS

- The distance of outermost electron from the nucleus of an atom while considering it spherical is called atomic radius.
- The size of atoms and ions decreases from left to right along the period. In a given period, the number of shells in all the elements remains the same. However, the value of effective nuclear charge increases from left to right due to increase in number of protons. The increased effective nuclear charge pulls the electron cloud of the atom closer to the nucleus. Thus, the size of the atoms and ions goes on decreasing from left to right.
- Along period the atomic and ionic radii of s-and p-block elements decrease with the increase of atomic number. This is shown in the table given below. The radii in the table are given in Å



Group Period	s-block elements		p-block elements				
	IA	IIA	IIIA	IVA	VA	VIA	VIIA
1	H 2.08 (+1) 0.29 (+1)						
2	Li 0.60 (+1)	Be 0.31 (+2)	B 0.20 (+3) 0.15 (+4)	C 2.60 (+4) 0.15 (+4)	N 1.71 (+3) 0.11 (+5)	O 1.40 (+2) 0.09 (+6)	F 1.36 (+1) 0.07 (+7)
3	Na 0.95 (+1)	Mg 0.65 (+2)	Al 0.50 (+3)	Si 2.71 (+1) 0.41 (+4)	P 2.12 (+3) 0.34 (+5)	S 1.84 (+2) 0.29 (+6)	Cl 1.81 (+1) 0.26 (+7)
4	K 1.33 (+1)	Ca 0.99 (+2)	Ga 1.13 (+1) 0.62 (+3)	Ge 0.93 (+2) 0.53 (+4)	As 2.22 (+3) 0.47 (+5)	Se 1.98 (+2) 0.42 (+6)	Br 1.95 (+1) 0.39 (+7)
5	Rb 1.48 (+1)	Sr 1.13 (+2)	In 1.32 (+1) 0.81 (+3)	Sn 1.12 (+2) 0.71 (+4)	Sb 0.45 (+3) 0.62 (+5)	Te 2.21 (+2) 0.56 (+6)	I 2.16 (+1) 0.50 (+7)
6	Cs 1.69 (+1)	Ba 1.35 (+2)	Tl 1.40 (+1) 0.95 (+3)	Pb 1.20 (+2) 0.84 (+4)	Bi 1.20 (+3) 0.74 (+5)	Po	At
7	Fr 1.76 (+1)	Ra 1.40 (+2)					

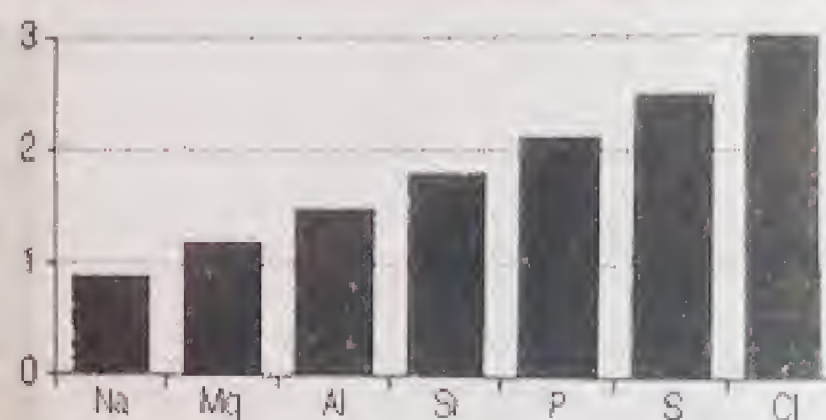
### (3) TRENDS IN ELECTRONEGATIVITY

#### Definition

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons.

#### Scale of Electronegativity

- The Pauling scale is the most commonly used.
- Fluorine is the most electronegative element. It is assigned a value of 4.0.
- The values range down to caesium and francium which are the least electronegative at 0.7.



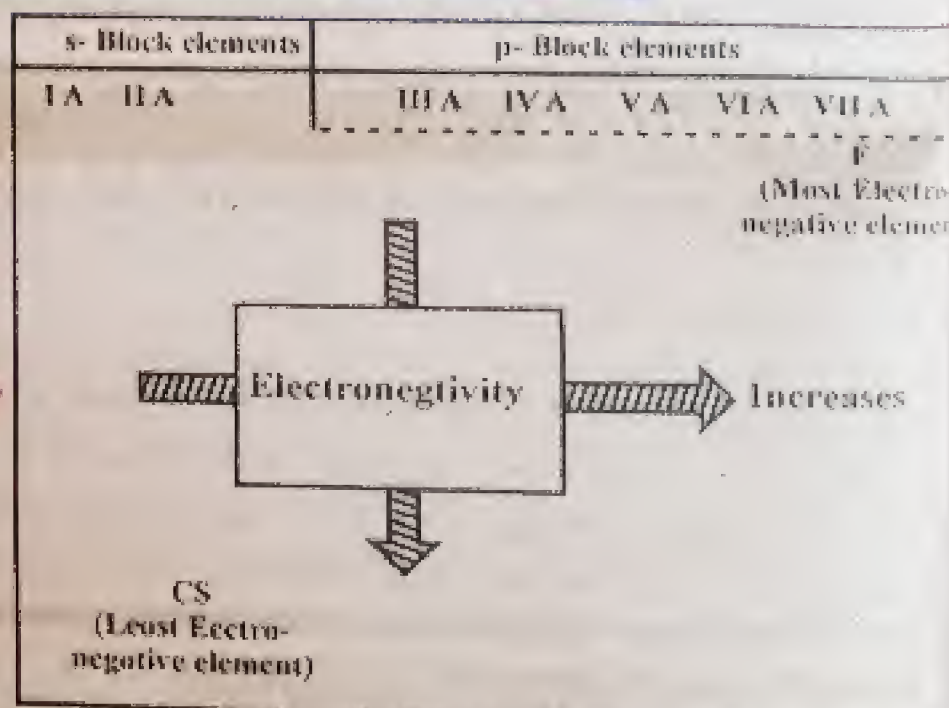
#### Trend or Variation in electronegativity along period:

The electronegative values increases from left to right in a period of s- and p-block elements.

It is due to following reasons.

- In a period, the atomic size decreases from left to right. Since, smaller atoms have greater tendency to attract the electrons towards themselves. Thus, smaller atoms have higher electronegativity values.
- In a period, values of ionization energy and electron affinity of the elements increase from left to right. Thus, the atoms of the elements with higher value of ionization energies and electron affinities also have higher electronegativities.

The variation of electronegativity in a period and a group of representative elements (s- and p-block elements) is show in the figure.



#### Electronegativity cannot be assigned to Argon

It is because electronegativity is the tendency of an atom to attract a bonding pair of electrons. Since argon does not form covalent bonds, electronegativity cannot be assigned to it.

#### Another Trend Explanation

- Along period from left to right, the bonding electrons are always in the same level. Thus, they are always being shielded by the same inner electrons. In period 3, it is the level 3.
- However, the number of protons in the nucleus increases from left to right. Thus, due to increase in nuclear charge, it attracts the bonding pair more closely. Hence, electronegativity increase from left to right.



## (B) PHYSICAL PROPERTIES

These properties depend upon the structure of elements.

### STRUCTURES OF THE ELEMENTS

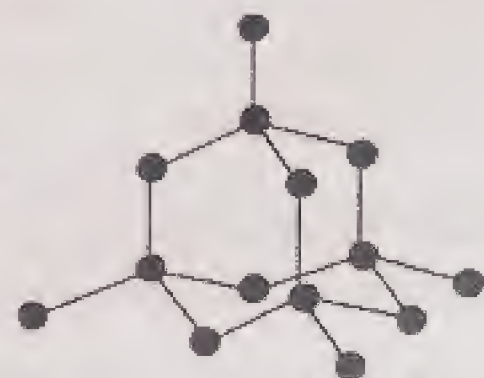
The structures of the elements changes along the period. In period 3, the first three (i.e. Na, Mg, Al) are metallic, silicon is giant covalent, and the remaining (i.e. P, S, Cl, Ar) are simple molecules.

#### (1) Three metallic structures

- Sodium, magnesium and aluminium all have metallic structures.
- In sodium, only one electron per atom is involved in the metallic bond i.e., the single 3s electron. In magnesium, both of its outer electrons are involved. In aluminium all three valence electrons are involved.
- The other difference is the way of packing of atoms in the metal crystal.
  - ✓ Sodium is 8-co-ordinated. Thus, each sodium atom is touched by only 8 other atoms.
  - ✓ Both magnesium and aluminium are 12-co-ordinated. However, both are packed in slightly different ways. This is a more efficient way to pack atoms. Thus, there less space is wasted in the metal structures and therefore, stronger bonding is present in the metal.

#### (2) A giant covalent structure

- Silicon has a giant covalent structure just like diamond as shown in the figure.
- The structure is held together by strong covalent bonds in all three dimensions.



#### (3) Four simple molecular structures

- The structures of phosphorus (i.e. white etc.) and sulphur (i.e. rhombic or monoclinic etc.) depends upon the allotropic forms of phosphorus or sulphur.
- The atoms in each of these molecules are held together by covalent bonds.
- In argon, there is no bond.
- In the liquid or solid state, the molecules are held close to each other by van der Waals dispersion forces.



a P<sub>4</sub> molecule



an S<sub>8</sub> molecule



a Cl<sub>2</sub> molecule



an Ar molecule

### (1) ELECTRICAL CONDUCTIVITY

- Sodium, magnesium and aluminium** are all good conductors of electricity. Among these conductivity increases from left to right (i.e., from sodium to magnesium to aluminium). It is because, the number of valence (free) electrons increases. Sodium has one, magnesium has two and aluminium has three valence electrons.
- Silicon** is a semiconductor.
- The rest elements of period 3 (**phosphorus, sulphur, chlorine and argon**) do not conduct electricity.

#### Explanation

- The three metals (Na, Mg, Al) conduct electricity. It is because the delocalized electrons (electrons sea) are free to move throughout the solid or the liquid metal.
- In the silicon case, the semiconductors conduct electricity depending upon conditions of temperature etc. Silicon has diamond like structure. So, it must be an insulator. But it is a semiconductor and its conductivity increases with increase in temperature.
- The remaining elements do not conduct electricity because they are simple molecular substances. They do not have free electrons to carry current.



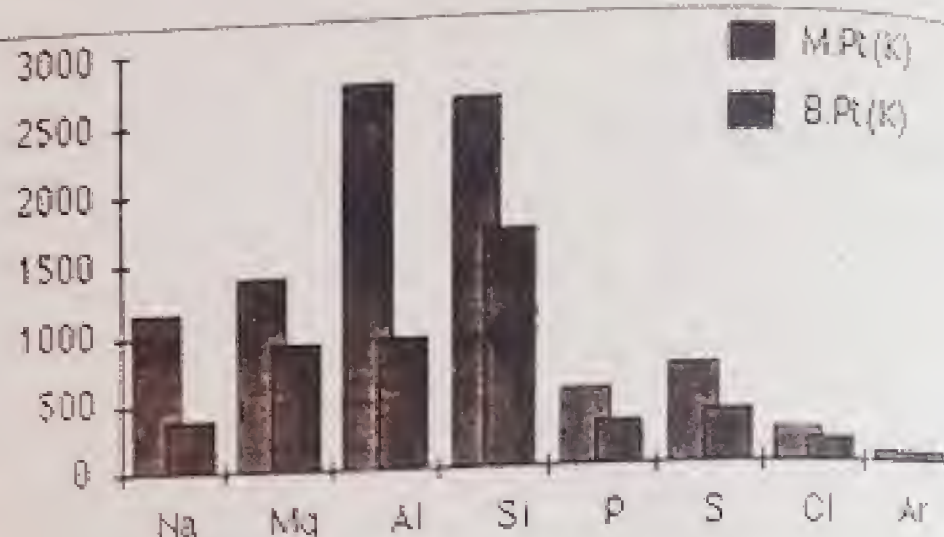
**Exercise Q3 (i) (d)** The melting and boiling points of the elements increase from left to right up to the middle in period 3 elements and decrease onward. Why?

## (2) TRENDS IN MELTING AND BOILING POINTS

- The figure shows the variation of melting and boiling points of the elements across the period 3.
- The melting and boiling points are given in Kelvin rather than  $^{\circ}\text{C}$  to avoid negative values.

### Sodium, Magnesium and Aluminium

They possess metallic structures. The melting point and boiling points increases from sodium to aluminium. It is because Na provides one valence electron for bonding, Mg provides two electrons and aluminium provides three electrons.



### Silicon

- Silicon has high melting and boiling points because it is a giant covalent structure. It has strong covalent bonds which are difficult to break.
- Since silicon has a different type of bonds so its melting and boiling points should not be directly compare with that of aluminium.

### The Four Molecular Elements

- Phosphorus, sulphur, chlorine and argon are simple molecular substances.
- These have only weak van der Waals forces between the molecules. Hence, their melting or boiling points are lower than those of the first four members of the period which have giant structures.
- The sizes of the melting and boiling points depends upon the sizes of the molecules. Generally, the melting and boiling points increase with increase in molecular size.



a  $\text{P}_4$  molecule



an  $\text{S}_8$  molecule



a  $\text{Cl}_2$  molecule



an Ar molecule

(not drawn to scale)

### Phosphorus

Phosphorus consists of  $\text{P}_4$  molecules. To melt phosphorus there is no need to break any covalent bonds. Only much weaker van der Waals forces between the molecules are broken. Thus, its melting point is low.

### Sulphur

Sulphur consists of  $\text{S}_8$  rings of atoms. So, its molecules are bigger (8 atoms) than phosphorus molecules (4 atoms). Hence, the van der Waals attractions will be stronger, leading to a higher melting and boiling point.

### Chlorine

Chlorine,  $\text{Cl}_2$ , is a much smaller molecule with comparatively weak van der Waals attractions. Hence, chlorine will have a lower melting and boiling point than sulphur or phosphorus.

### Argon

Argon molecules are just single argon atoms, Ar. They have limited and very weak van der Waals forces. Hence, the melting and boiling points of argon are lower again.



## QUICK QUIZ-2

- a) Write down the symbols of the elements in the third period of the periodic table (ending with the noble gas, argon) in order of increasing atomic number.  
The elements are: Sodium (Na), Magnesium (Mg), Aluminium (Al), Silicon (Si), Phosphorus (P), Sulphur (S), Chlorine (Cl) and Argon (Ar).
- b) Which of these elements are  
(i) s-block elements: Sodium (Na) and Magnesium (Mg). Since, both these have their valence electrons in s-orbital.  
(ii) p-block elements: Aluminium (Al), Silicon (Si), Phosphorus (P), Sulphur (S), Chlorine (Cl) and Argon (Ar). Since all these have their valence electrons in p-orbital.  
(iii) d-block elements: There are no d-block elements in Period 3, since none of the period 3 elements have valence electron in d-orbital.
- c) (i) Write the empirical formula of the chloride formed by the elements of atomic number 13.  
Element with atomic number 13 is Aluminium (Al). Thus the formula of its chloride is  $\text{AlCl}_3$ .  
However, it can exist in dimeric form,  $\text{Al}_2\text{Cl}_6$ , as well.
- (ii) Describe briefly how you could prepare a sample of this chloride.  
The aluminium burns in the stream of chlorine to produce very pale yellow aluminium chloride.  
$$2\text{Al} + 3\text{Cl}_2 \rightarrow 2\text{AlCl}_3$$

## (C) CHEMICAL REACTIONS OF THE PERIOD 3 ELEMENTS

The reactions of Period 3 elements are given below.

Exercise Q3 (i) (c): Describe the trends in reaction of period 3 elements with water.

### 1) REACTIONS WITH WATER

#### Sodium

- Sodium has a very exothermic reaction with cold water producing hydrogen gas and a colourless solution of sodium hydroxide. The reaction is so much exothermic that the liberated hydrogen catches fire.

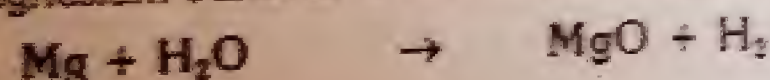


#### Magnesium

- Magnesium has a very slight reaction with cold water, but burns in steam.
- A very clean coil of magnesium dropped into cold water finally gets covered by small bubbles of hydrogen which float it to the surface.
- Magnesium hydroxide is formed as a very thin layer on the magnesium. It acts as a protective layer and thus tends to stop the reaction.



- Magnesium burns in steam with its typical white flame to produce white magnesium oxide and hydrogen.



#### Aluminium

- When Aluminium powder is heated in steam, it produces hydrogen and aluminium oxide.
- The reaction is relatively slow because of the strong aluminium oxide layer on the metal and formation of more oxide during the reaction. The oxide layer acts as a protective layer and thus slows down the reaction.



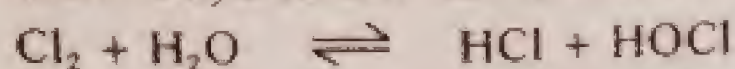
#### Phosphorus and sulphur

These have no reaction with water.



### Chlorine

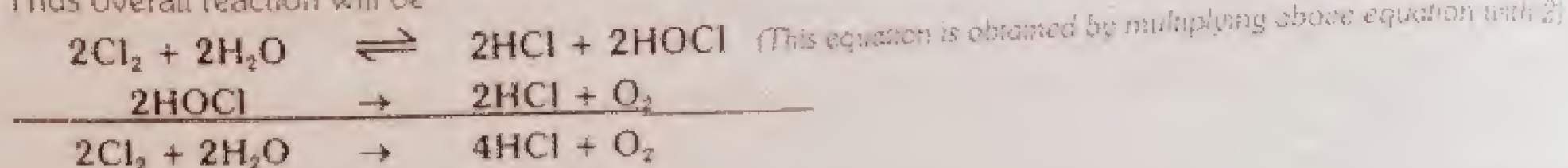
- Chlorine dissolves in water to some extent to give a green solution. A reversible reaction takes place to produce a mixture of hydrochloric acid and chloric(I) acid (hypochlorous acid).



- In the presence of sunlight, the chloric(I) acid slowly decomposes to produce more hydrochloric acid, releasing oxygen gas.



- Thus overall reaction will be



### Argon

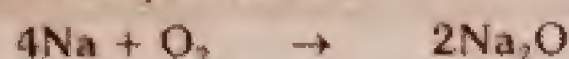
There is no reaction between argon and water

## **(2) REACTIONS WITH OXYGEN**

### Sodium

- Sodium burns in oxygen with an orange flame to produce a white solid mixture of sodium oxide and sodium peroxide.

For the simple oxide



For the peroxide



### Magnesium

Magnesium burns in oxygen with an intense white flame to give white solid magnesium oxide.



### Silicon

Silicon will burn in oxygen if heated strongly. Silicon dioxide is produced.



### Phosphorus

- White phosphorus catches fire spontaneously in air. It burns with a white flame and producing clouds of white smoke which is a mixture of phosphorus(III) oxide and phosphorus(V) oxide.

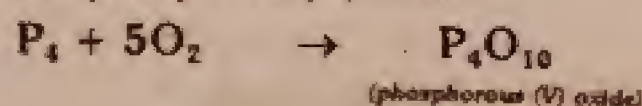
The proportions of two oxides depend on the amount of oxygen available.

- In an excess of oxygen, the product will be almost completely phosphorus (V) oxide.

For the phosphorus(III) oxide:

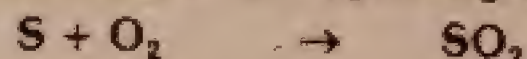


For the phosphorus(V) oxide:



### Sulphur

- Sulphur burns in air or oxygen on gentle heating with a pale blue flame. It produces colourless sulphur dioxide gas.



### Chlorine and argon

- Despite having several oxides, chlorine won't react directly with oxygen. Argon does not react either.



### Properties of the oxides of elements in Period 3

Formula of Oxide →	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>4</sub> O <sub>10</sub> (P <sub>2</sub> O <sub>5</sub> )	SO <sub>2</sub> (SO <sub>2</sub> )	Cl <sub>2</sub> O <sub>7</sub> (Cl <sub>2</sub> O)
State of Oxide	solid	solid	solid	solid	solid	liquid	liquid
Conduction of Electricity by Molten or liquid Oxide	good	good	good	poor	No	No	No
Structure of oxide	Crystalline				Single molecular		
Enthalpy change of Formation of oxide at 298K/kJ mol <sup>-1</sup>	-416	-602	-1676	-923	-2984	-395	82
Enthalpy change of Formation of oxide at 298K/kJ mol <sup>-1</sup>	-416	-602	-1676	-923	-2984	-395	82
Effect of adding oxide to water	reacts to form NaOH (aq) Alkaline solution	reacts to form Mg(OH) <sub>2</sub>	does not react with water but is amphoteric	does not react with water but is acidic	P <sub>4</sub> O <sub>10</sub> reacts to form H <sub>2</sub> PO <sub>4</sub> (acid solution)	SO <sub>2</sub> reacts to form H <sub>2</sub> SO <sub>3</sub> (acid solution)	Cl <sub>2</sub> O <sub>7</sub> reacts to form HClO <sub>4</sub> (acid solution)
Nature of Oxide	Basic (alkaline)	Basic (weakly alkaline)	Amphoteric	Acidic	Acidic	Acidic	Acidic

### (3) REACTIONS WITH CHLORINE

#### Sodium

- Sodium burns in chlorine with a bright orange flame. White solid sodium chloride is produced.



#### Magnesium

- Magnesium burns with its intense white flame to give white magnesium chloride.



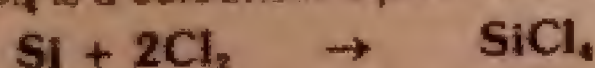
#### Aluminium

- Aluminium is often reacted with chlorine by passing dry chlorine over aluminium foil heated in a long tube.
- The aluminium burns in the stream of chlorine to produce very pale yellow aluminium chloride. This sublimes (direct conversion from solid to vapour) and collects in the cooler part of the tube.



#### Silicon

- When chlorine is passed over silicon powder heated in a tube, it reacts to produce silicon tetrachloride.
- SiCl<sub>4</sub> is a colourless liquid which vaporises and can be condensed further along the apparatus.



#### Phosphorus

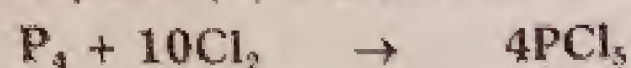
- White phosphorus burns in chlorine to produce a mixture of two chlorides, phosphorus(III) chloride and phosphorus(V) chloride (phosphorus trichloride, PCl<sub>3</sub> and phosphorus pentachloride, PCl<sub>5</sub>).
- Phosphorus(III) chloride is a colourless fuming liquid.





CH # 13: s and p-Block Elements

- Phosphorus(V) chloride is an off-white (going towards yellow) solid.



**Sulphur**

- When a stream of chlorine is passed over some heated sulphur, it reacts to form an orange, evil-smelling liquid, disulphur dichloride,  $\text{S}_2\text{Cl}_2$ .



**Chlorine and Argon**

- Chlorine gas ( $\text{Cl}_2$ ) cannot react with itself.
- Argon does not react with chlorine.

## (D) PHYSICAL PROPERTIES OF THE OXIDES

- The relationship between the physical properties of the oxides of Period 3 elements (sodium to chlorine) and their structures is given below.
- Argon is omitted because it does not form an oxide.

## THE OXIDES

The important oxides of Period 3 elements are:

$\text{Na}_2\text{O}$	$\text{MgO}$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{P}_4\text{O}_{10}$	$\text{SO}_3$	$\text{Cl}_2\text{O}_7$
				$\text{P}_4\text{O}_6$	$\text{SO}_2$	$\text{Cl}_2\text{O}$

- Those oxides in the first row are known as the **highest oxides** of the various elements. i.e. In these oxides, Period 3 elements are in their highest oxidation states.
- In highest oxides, all the valence electrons in the Period 3 element are involved in the bonding.  
e.g. one electron for sodium, two for magnesium, three for aluminium and so on.

## (i) STRUCTURES OF OXIDES

The trend in structure changes from the metallic oxides containing giant structures of ions on the left of the period via a giant covalent oxide (silicon dioxide) in the middle to molecular oxides on the right.

### (i) The metallic oxides (e.g Sodium, Magnesium, aluminium etc.)

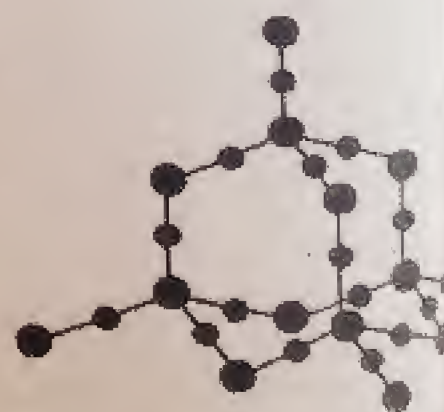
- Sodium, magnesium and aluminium oxides structure/diagram is same as sodium chloride. i.e. They exist as ionic crystalline solids.

### (ii) Giant Covalent Oxides [e.g Silicon dioxide (silicon(IV) oxide)]

- Crystalline silicon has the same structure as diamond. In this structure atoms of both silicon and oxygen are present.
- In  $\text{SiO}_2$ , each silicon atom is bridged to its neighbouring silicon by an oxygen atom.

### (iii) The molecular oxides

(e.g. Phosphorus, sulphur and chlorine oxides)



## (A) THE PHOSPHORUS OXIDES

Phosphorus has two common oxides,

(i) Phosphorus(III) oxide,  $\text{P}_4\text{O}_6$

(ii) Phosphorus(V) oxide,  $\text{P}_4\text{O}_{10}$

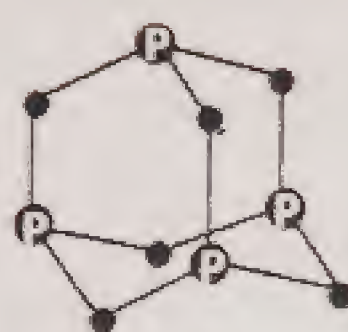


a  $\text{P}_4$  molecule

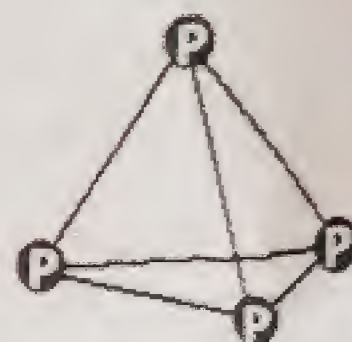


### (I) PHOSPHORUS(III) OXIDE ( $P_4O_6$ )

- It is a white solid
- Its melting point is  $24^\circ\text{C}$
- Its boiling point is  $173^\circ\text{C}$ .
- The structure of  $P_4O_6$  can be obtained starting from a  $P_4$  molecule which is a little tetrahedron.
  - ✓ Pull  $P_4$  structure apart to see the bonds
  - ✓ Then link all the phosphorus atoms via oxygen atoms. These will be in a V-shape structure (like in water).
- The phosphorus is using only three of its outer electrons (the unpaired p electrons) to form bonds with the oxygens.

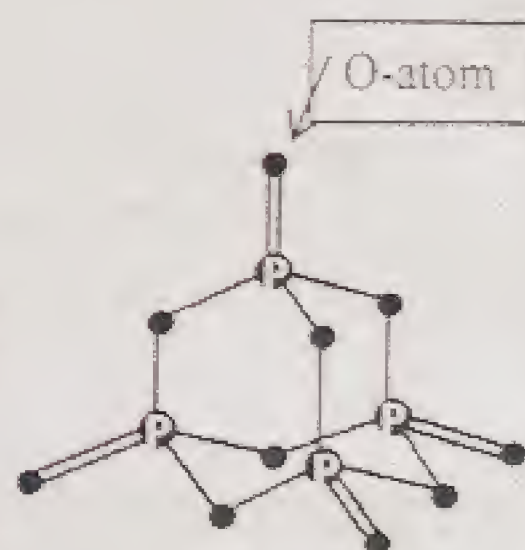


1  $P_4$  molecule



1  $P_4$  molecule

3



1  $P_4O_6$  molecule

### (II) PHOSPHORUS(V) OXIDE ( $P_4O_{10}$ )

- It is a white solid
- It sublimes (turning straight from solid to vapour) at  $300^\circ\text{C}$ .
- Solid phosphorus(V) oxide exists in several different forms. Some of these are polymeric. The most common is the simple molecular form. This is also present in the vapour.
- In this oxide, the phosphorus uses all five of its outer electrons in the bonding.
- This is most easily drawn starting from  $P_4O_6$ . The other four oxygens are attached to the four phosphorus atoms via double bonds.

## 3) THE SULPHUR OXIDES

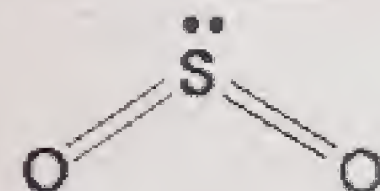
Sulphur has two common oxides

(I) Sulphur dioxide (sulphur(IV) oxide),  $SO_2$ .

(II) Sulphur trioxide (sulphur(VI) oxide),  $SO_3$ .

### (I) SULPHUR DIOXIDE ( $SO_2$ )

- It is a colourless gas at room temperature.
- It has choking smell which can be recognised easily.
- It consists of simple  $SO_2$  molecules.
- The sulphur uses 4 of its outer electrons to form the double bonds with the oxygen, leaving the other two as a lone pair on the sulphur.
- The bent shape of  $SO_2$  is due to this lone pair.



Remember! (the similar explanation can be given for P as well)

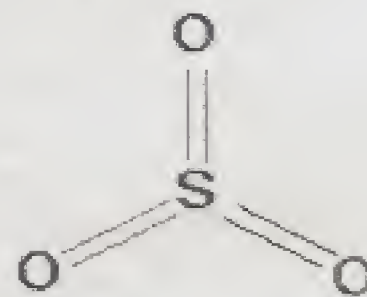
S (ground state)	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$
	3s	3p <sub>x</sub>	3p <sub>y</sub>	3p <sub>z</sub>	3d <sub>xy</sub>	3d <sub>xz</sub>	3d <sub>yz</sub>	3d <sub>z^2</sub>	3d <sub>x^2-y^2</sub>
if one electron jumps then		$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$				
	3s	3p <sub>x</sub>	3p <sub>y</sub>	3p <sub>z</sub>	3d <sub>xy</sub>	3d <sub>xz</sub>	3d <sub>yz</sub>	3d <sub>z^2</sub>	3d <sub>x^2-y^2</sub>
	(one pair)								
if Second electron jumps then		$\uparrow$	$\uparrow$	$\uparrow$	$\uparrow$				
	3s	3p <sub>x</sub>	3p <sub>y</sub>	3p <sub>z</sub>	3d <sub>xy</sub>	3d <sub>xz</sub>	3d <sub>yz</sub>	3d <sub>z^2</sub>	3d <sub>x^2-y^2</sub>

Four unpaired electrons, so four bonds are formed

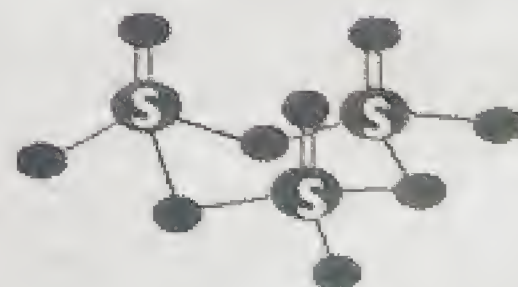
Six unpaired electrons, so six bonds are formed

### (II) SULPHUR TRIOXIDE ( $SO_3$ )

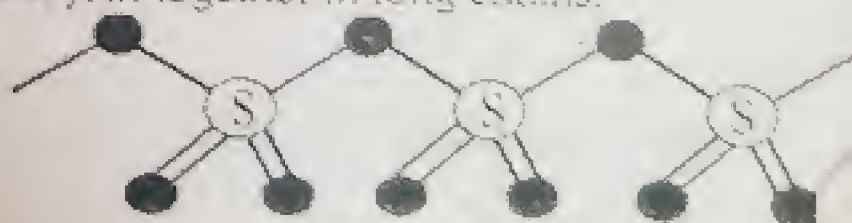
- It is a white solid
- It has low melting and boiling point.
- Gaseous sulphur trioxide consists of simple  $SO_3$  molecules in which all six of the sulphur's outer electrons are involved in the bonding.



- There are various forms of solid sulphur trioxide. The simplest one is a trimer,  $S_3O_9$ , where three  $SO_3$  molecules are joined up and arranged in a ring.



- There are also other polymeric forms in which the  $SO_3$  molecules join together in long chains. So, the simple molecules join up in this way to make bigger structures. Thus, it makes the sulphur trioxide a solid rather than a gas.





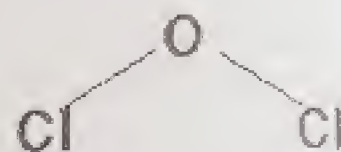
## (C) THE CHLORINE OXIDES

Chlorine forms several oxides. Two are important

- (i) Chlorine(I) oxide,  $\text{Cl}_2\text{O}$ ,
- (ii) Chlorine(VII) oxide,  $\text{Cl}_2\text{O}_7$ .

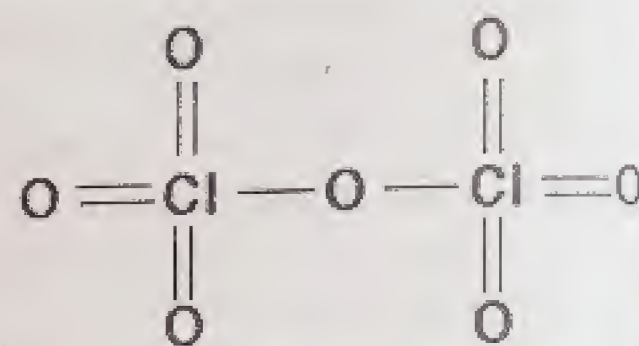
### (i) CHLORINE(I) OXIDE ( $\text{Cl}_2\text{O}$ )

- It is a yellowish-red gas at room temperature.
- It consists of simple small molecules.
- In this structure chlorine uses its one outer electron and bonds with oxygen.



### (ii) CHLORINE(VII) OXIDE ( $\text{Cl}_2\text{O}_7$ )

- It is a colourless oily liquid at room temperature.
- In chlorine(VII) oxide, the chlorine uses all of its seven outer electrons and bonds with oxygen. This produces a much bigger molecule.



## (ii) MELTING AND BOILING POINTS

- The giant structures (the metal oxides and silicon dioxide) will have high melting and boiling points. It is because a lot of energy is needed to break the strong bonds (ionic or covalent) operating in three dimensions.
- The oxides of phosphorus, sulphur and chlorine consist of individual molecules. Some are small and simple, others polymeric.
- The attractive forces between these molecules will be van der Waals dispersion and dipole-dipole interactions. These vary depending on the size, shape and polarity of the various molecules. However, these forces are always much weaker than the ionic or covalent bonds of a giant structure. Thus, these oxides tend to be gases, liquids or low melting point solids.

## (iii) ELECTRICAL CONDUCTIVITY

- None of these oxides has any free or mobile electrons. Thus, none of them will conduct electricity when they are solid.
- The ionic oxides can conduct electricity in molten state. It is because the ions become free in molten state. So, the movement of the ions towards the electrodes causes electrical conductivity. Thus, they undergo **electrolysis** when they are molten.

## (iv) ACID-BASE BEHAVIOUR OF THE OXIDES

The reactions of the oxides of Period 3 elements (sodium to chlorine) with water and with acids or bases shows their acid-base behaviour.

### (A) TREND IN ACID-BASE BEHAVIOUR

A brief summary is given below

- Generally, basicity of oxides decreases and acidity increases from left to right
- The increasing acidic order from left to right is shown in Period 3 oxides.

$\text{Na}_2\text{O}$   
Strongly  
Basic

$\text{MgO}$   
Basic

$\text{Al}_2\text{O}_3$   
Amphoteric

$\text{SiO}_2$   
Weakly  
Acidic

$\text{P}_2\text{O}_5$   
Acidic

$\text{SO}_2$   
Strongly  
Acidic

$\text{Cl}_2\text{O}_7$   
Very  
strongly acidic

- An amphoteric oxide is one which shows both acidic and basic properties.



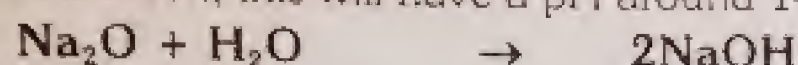
## REACTIONS OF OXIDES WITH WATER, ACIDS AND BASES: CHEMISTRY OF THE INDIVIDUAL OXIDES

### SODIUM OXIDE ( $\text{Na}_2\text{O}$ )

Sodium oxide is a simple strongly basic oxide. It is basic because it contains the oxide ion,  $\text{O}^{2-}$ , which is a very strong base with a high tendency to combine with hydrogen ions.

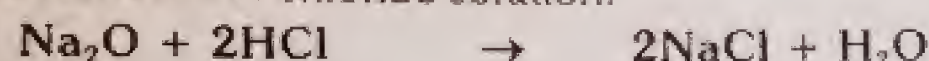
#### Reaction with water

Sodium oxide reacts exothermically with cold water to produce sodium hydroxide solution. Depending on its concentration, this will have a pH around 14.



#### Reaction with acids

As a strong base, sodium oxide also reacts with acids. e.g., it would react with dilute hydrochloric acid to produce sodium chloride solution.

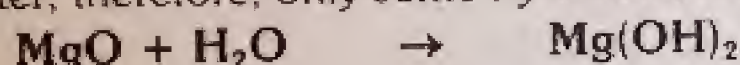


### MAGNESIUM OXIDE ( $\text{MgO}$ )

- Magnesium oxide is a simple basic oxide, because it also contains oxide ions.
- However, it is less basic than sodium oxide because the oxide ions are not much free.
- In the sodium oxide case, the solid is held together by attractions between  $1+$  ( $\text{Na}^+$ ) and  $2-$  ( $\text{O}^{2-}$ ) ions. In the magnesium oxide case, the attractions are between  $2+$  ( $\text{Mg}^{2+}$ ) and  $2-$  ( $\text{O}^{2-}$ ). Thus, it takes more energy to break these. So, it is a relatively a weaker base.

#### Reaction with water

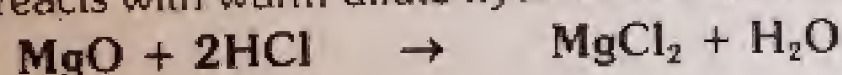
- If some white magnesium oxide powder is shaken with water, apparently no reaction occurs.
- However, the pH of the liquid goes around pH 9 showing that solution has become slightly alkaline.
- It shows that there must have been some slight reaction with the water to produce hydroxide ions in solution. Some magnesium hydroxide is formed in the reaction. Since,  $\text{Mg}(\text{OH})_2$  is almost insoluble in water, therefore, only some hydroxide ions actually go into the solution and it becomes slightly alkaline.



#### Reaction with acids

Magnesium oxide reacts with acids to produce salts.

e.g. It reacts with warm dilute hydrochloric acid to give magnesium chloride solution.



### ALUMINIUM OXIDE ( $\text{Al}_2\text{O}_3$ )

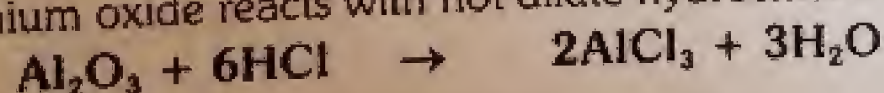
It is an amphoteric oxide. It gives reactions as both a base and an acid.

#### Reaction with water

Aluminium oxide does not react in a simple way with water and does not dissolve in it. Although it still contains oxide ions, they are held too strongly in the solid lattice to react with the water.

#### Reaction with acids

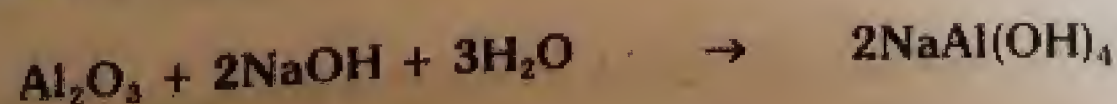
Aluminium oxide reacts with hot dilute hydrochloric acid to give aluminium chloride solution.



#### Reaction with bases

Aluminium oxide also shows acidic nature, as reacts with bases such as sodium hydroxide solution.

- By this reaction various aluminates are formed. Aluminates are compounds where the aluminium is found in the negative ion. This is possible because aluminium has the ability to form covalent bonds with oxygen.
- With hot, concentrated sodium hydroxide solution, aluminium oxide reacts to give a colourless solution of sodium tetrahydroxoaluminate.





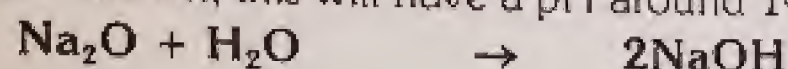
**(B) REACTIONS OF OXIDES WITH WATER, ACIDS AND BASES: CHEMISTRY OF THE INDIVIDUAL OXIDES**

**SODIUM OXIDE ( $\text{Na}_2\text{O}$ )**

Sodium oxide is a simple strongly basic oxide. It is basic because it contains the oxide ion,  $\text{O}^{2-}$ , which is a very strong base with a high tendency to combine with hydrogen ions.

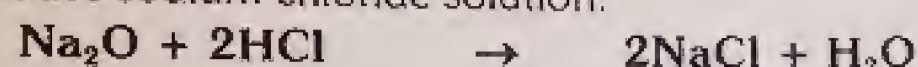
**Reaction with water**

Sodium oxide reacts exothermically with cold water to produce sodium hydroxide solution. Depending on its concentration, this will have a pH around 14.



**Reaction with acids**

As a strong base, sodium oxide also reacts with acids. e.g., it would react with dilute hydrochloric acid to produce sodium chloride solution.

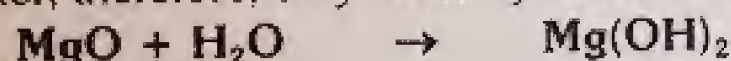


**MAGNESIUM OXIDE ( $\text{MgO}$ )**

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**Reaction with water**

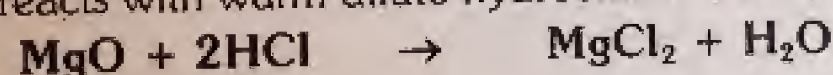
- If some white magnesium oxide powder is shaken with water, apparently no reaction occurs.
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- It shows that there must have been some slight reaction with the water to produce hydroxide ions in solution. Some magnesium hydroxide is formed in the reaction. Since,  $\text{Mg}(\text{OH})_2$  is almost insoluble in water, therefore, only some hydroxide ions actually go into the solution and it becomes slightly alkaline.



**Reaction with acids**

Magnesium oxide reacts with acids to produce salts.

e.g. It reacts with warm dilute hydrochloric acid to give magnesium chloride solution.



**ALUMINIUM OXIDE ( $\text{Al}_2\text{O}_3$ )**

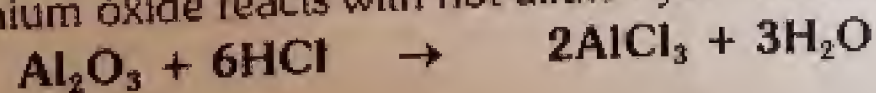
It is an amphoteric oxide. It gives reactions as both a base and an acid.

**Reaction with water**

Aluminium oxide does not react in a simple way with water and does not dissolve in it. Although it still contains oxide ions, they are held too strongly in the solid lattice to react with the water.

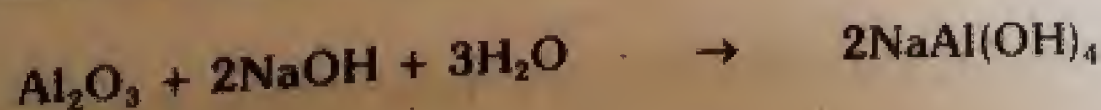
**Reaction with acids**

Aluminium oxide reacts with hot dilute hydrochloric acid to give aluminium chloride solution.



**Reaction with bases**

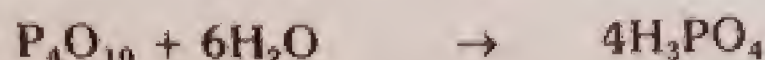
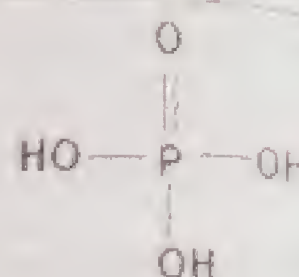
- Aluminium oxide also shows acidic nature, as reacts with bases such as sodium hydroxide solution.
- By this reaction various aluminates are formed. Aluminates are compounds where the aluminium is found in the negative ion. This is possible because aluminium has the ability to form covalent bonds with oxygen.
- With hot, concentrated sodium hydroxide solution, aluminium oxide reacts to give a colourless solution of sodium tetrahydroxoaluminate.



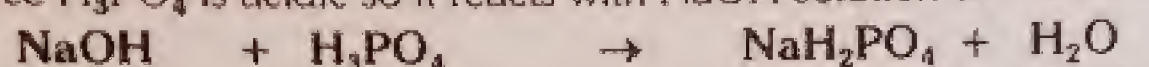


**PHOSPHORUS(V) OXIDE ( $P_4O_{10}$ )****Reaction with Water**

Phosphorus(V) oxide reacts violently with water to give a solution containing a mixture of acids, the nature of which depends on the conditions. Consider one of these, phosphoric(V) acid,  $H_3PO_4$  (also known just as phosphoric acid or as orthophosphoric acid).

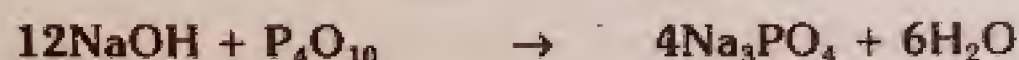
**Reaction with Base:**

Since  $H_3PO_4$  is acidic so it reacts with NaOH solution as follows.

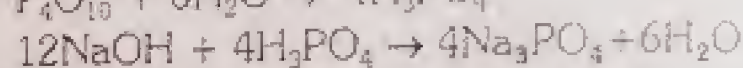
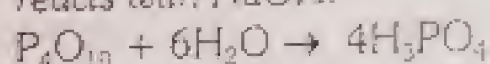


If phosphorus(V) oxide is reacted directly with sodium hydroxide solution then same possible salts are obtained.

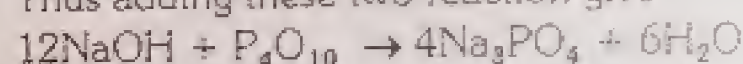
e.g.,

**Remember!**

The  $P_4O_{10}$  first reacts with water to produce  $H_3PO_4$  in solution which then reacts with NaOH.



Thus adding these two reaction give

**THE SULPHUR OXIDES ( $SO_2$ )**

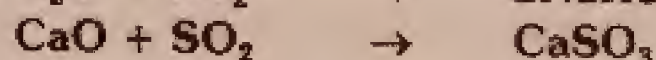
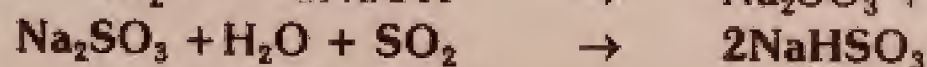
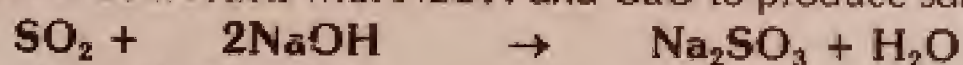
Two oxides are more important: sulphur dioxide,  $SO_2$ , and sulphur trioxide,  $SO_3$ .

**SULPHUR DIOXIDE****Reaction with Water:**

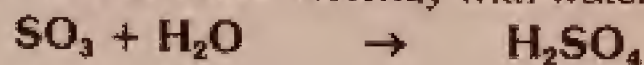
Sulphur dioxide is fairly soluble in water, reacting with it to give a solution of sulphurous acid,  $H_2SO_3$ .

**Reaction with Base:**

Since it is acidic so it reacts with NaOH and CaO to produce salts.

**SULPHUR TRIOXIDE**

- Sulphur trioxide reacts violently with water to produce a fog of concentrated sulphuric acid droplets.

**Reaction with Base:**

- $SO_3$  reacts with NaOH aqueous solution to give  $Na_2SO_4$



- In principle, sodium hydrogensulphate ( $NaHSO_4$ ) can be obtained by using half mole sodium hydroxide so that only one acidic hydrogen of  $H_2SO_4$  is used.
- Sulphur trioxide itself will also react directly with bases to form sulphates. e.g. it will react with calcium oxide to form calcium sulphate.

**THE CHLORINE OXIDES ( $Cl_2O_n$ )**

- Chlorine forms several oxides, but two are more important, chlorine(VII) oxide,  $Cl_2O_7$ , and chlorine(I) oxide,  $Cl_2O$ .
- Chlorine(VII) oxide is also known as dichlorine heptoxide, and chlorine(I) oxide as dichlorine monoxide.

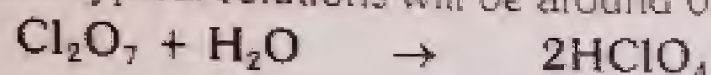


### CHLORINE(VII) OXIDE

- Chlorine(VII) oxide is the highest oxide of chlorine. It means that the chlorine is in its maximum oxidation state of +7.
- It has same trend of the highest oxides of the Period 3 elements. Thus, it shows to be a very strongly acidic.

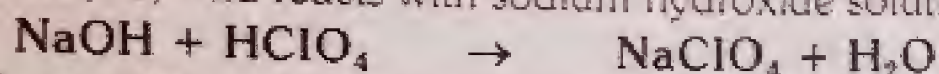
#### Reaction with Water:

- Chlorine(VII) oxide reacts with water to give the very strong acid, chloric(VII) acid. It is also known as perchloric acid.
- The pH of typical solutions will be around 0 just like sulphuric acid..

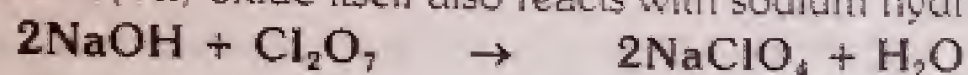


#### Reaction with Base:

- Chloric(VII) acid reacts with sodium hydroxide solution to form a solution of sodium chlorate(VII).



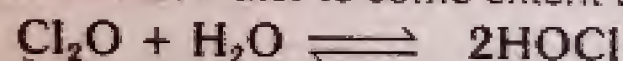
- Chlorine(VII) oxide itself also reacts with sodium hydroxide solution to give the same product.



### CHLORINE(I) OXIDE

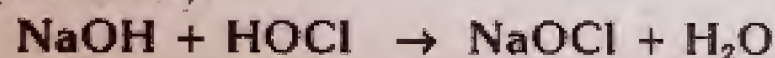
#### Reaction with Base:

- Chlorine(I) oxide is far less acidic than chlorine(VII) oxide.
- It reacts with water to some extent to give chloric(I) acid, HOCl. It is also known as hypochlorous acid.



#### Reaction with Base:

- Chloric(I) acid reacts with sodium hydroxide solution to give a solution of sodium chlorate(I) (sodium hypochlorite).



- Chlorine(I) oxide also reacts directly with sodium hydroxide to give the same product.



## **QUICK QUIZ-3**

(a) What is the nature of bonds in the oxides formed when Na, Mg, Al and S react with excess oxygen?

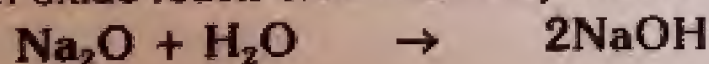
Na, Mg and Al form ionic oxides. Therefore, they exist as ionic crystalline structure.

S forms  $\text{SO}_2$  and  $\text{SO}_3$  with oxygen. These oxides have covalent bonding in them.

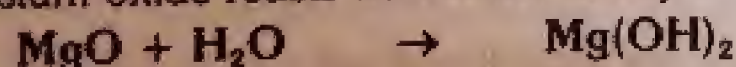
(b) How do these oxides react with

(i) Water

Sodium oxide reacts exothermically with cold water to produce sodium hydroxide solution.

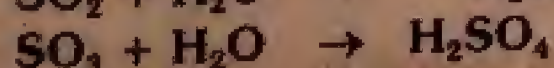
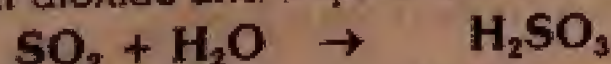


Magnesium oxide reacts with water slowly to produce alkaline solution.



Aluminium oxide does not react with water. It is due to the protective coating on it which prevents it from reaction. Or the reaction may be very very slow.

Sulphur dioxide and sulphur trioxide react with water to produce  $\text{H}_2\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  respectively.



(ii) Dilute acids

Sodium oxide is a strong base. So, it reacts with acids to form salts

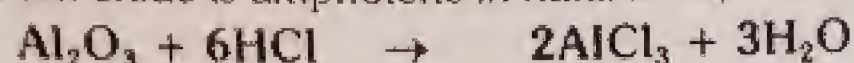




Magnesium oxide is basic in nature. So, it reacts with acids to form salts.

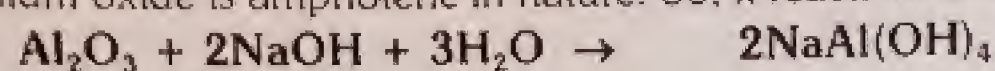


Aluminium oxide is amphoteric in nature. So, it reacts with acids to form salts.

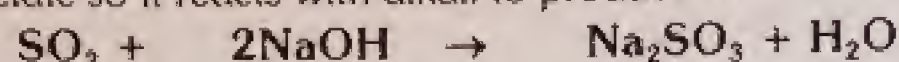


### (iii) Alkali

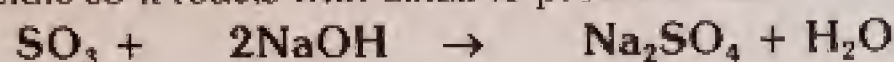
Aluminium oxide is amphoteric in nature. So, it reacts with alkali to form salt.



Since  $\text{SO}_2$  is acidic so it reacts with alkali to produce salts.



Since  $\text{SO}_3$  is acidic so it reacts with alkali to produce salts.



(c) **Magnesium chloride is a high melting point solid, aluminium chloride is a solid which sublimes readily at about  $180^\circ\text{C}$  and silicon tetrachloride is a volatile liquid. Explain the nature of the chemical bonding in these chlorides and show how this accounts for the above differences in volatility.**

- Magnesium chloride is an ionic solid in which ions are held together by strong ionic bonds. So, lots of energy is needed to break these strong forces. Thus, it has high melting point.
- At room temperature, solid aluminium chloride has an ionic lattice with a lot of covalent character. At temperatures around  $180 - 190^\circ\text{C}$ , aluminium chloride converts to a molecular form,  $\text{Al}_2\text{Cl}_6$ . So, now it has weak intermolecular forces. Hence, it melts or sublime easily.
- Silicon tetrachloride is a simple covalent chloride. The electronegativity difference between the silicon and the chlorine is very small to form ionic bonds. Thus, the only attractions between the molecules are van der Waals dispersion forces. So, it is a volatile liquid.

### Important!

### (Important Concept, Not in Syllabus)

#### Solubility of Salts in Water

The solubility of salts in water is mostly controlled by two factors

##### (i) Lattice Energy:

**Briefly, It is the amount of energy required to break the crystal lattice of a salt.**

- Generally, higher the lattice energy, lower the solubility and vice versa.
- Small size ions show tight packing, therefore, their salts possess high lattice energies and as a result have low solubilities.

##### (ii) Hydration Energy:

**Briefly, It is the amount of energy released when one mole of an ion dissolves in water to form infinite dilute solution.**

- Generally, higher the hydration energy of ions of a salt, higher the solubility of salt.
- Small size ions dissolve easily in water, therefore, they possess high hydration energies and as a result, their salts have high solubilities.

These two factors work opposite to each other, therefore,

- In one condition, lattice energy overcomes hydration energy and thus controls the solubility.  
e.g., in case of hydroxides of alkaline earth metals.
- In other condition, hydration energy overcomes lattice energy and thus controls the solubility.  
e.g., in case of sulphates of alkaline earth metals.



## (E) CHLORIDES OF THE PERIOD 3 ELEMENTS

### (I) THE STRUCTURES

- Sodium chloride and magnesium chloride are ionic. These consist of giant ionic lattices at room temperature
- Aluminium chloride and phosphorus(V) chloride change their structure from ionic to covalent when the solid turns to a liquid or vapour.
- The others are simple covalent molecules.

### (II) MELTING AND BOILING POINTS

- Sodium and magnesium chlorides are solids with high melting and boiling points. It is because they have strong ionic attractions and a large amount of heat is needed to break them.
- The rest are liquids or low melting point solids except aluminium chloride and phosphorus(V) chloride.
- In these the situation is quite complicated, the attractions in the others will be much weaker intermolecular forces such as van der Waals dispersion forces
- These vary depending on the size and shape of the molecule, but will always be far weaker than ionic bonds.

### (III) ELECTRICAL CONDUCTIVITY

- Sodium and magnesium chlorides are ionic and so will undergo **electrolysis** when they are molten.
- Electricity is carried by the movement of the ions and their discharge at the electrodes.
- In the aluminium chloride and phosphorus(V) chloride cases, the solid does not conduct electricity because the ions are not free to move. In the liquid (where it exists - both of these sublime at ordinary pressures), they have converted into a covalent form, and so don't conduct either.
- The rest of the chlorides don't conduct electricity either solid or molten because they don't have any ions or any mobile electrons.

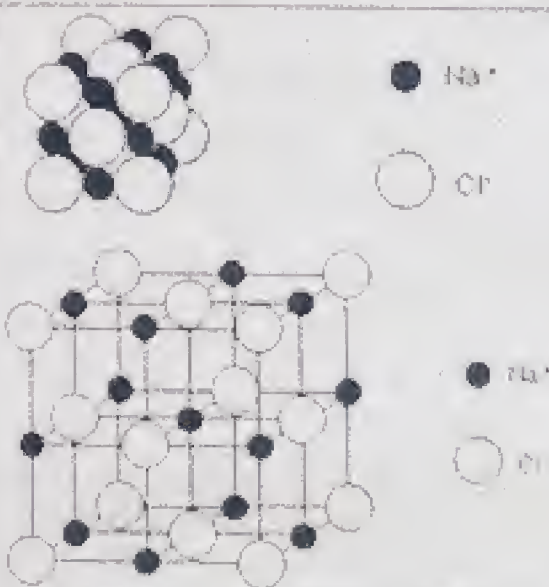
### (iv) REACTIONS WITH WATER

- Sodium and magnesium chloride just dissolve in water.
- The other chlorides all react with water in different ways.
- The reaction with water is known as **hydrolysis**.

## THE INDIVIDUAL CHLORIDES

### SODIUM CHLORIDE, NaCl

- Sodium chloride is a simple ionic compound consisting of a giant array of sodium and chloride ions as shown in the figure.
- The strong attractions between the positive and negative ions need a lot of heat energy to break. Thus, sodium chloride has high melting and boiling points.
- It does not conduct electricity in the solid state because it has not any mobile electrons and the ions are not free to move.
- However, when it melts it undergoes electrolysis.
- Sodium chloride simply dissolves in water to give a neutral solution.



### MAGNESIUM CHLORIDE, MgCl<sub>2</sub>

- Magnesium chloride is also ionic, but with a more complicated arrangement of the ions to allow for having twice as many chloride ions as magnesium ions.
- Again, lots of heat energy is needed to overcome the attractions between the ions, and so the melting and boiling points are again high.
- Solid magnesium chloride is a non-conductor of electricity because the ions are not free to move.
- However, it undergoes electrolysis when the ions become free on melting.

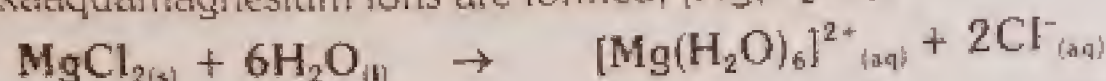


CH # 13: s and p-Block Elements

18

- Magnesium chloride dissolves in water to give a faintly acidic solution (pH = approximately 6)
- When magnesium ions are broken off the solid lattice and go into solution, there is enough energy between the  $2+$  ions and the water molecules to get co-ordinate (dative covalent) bonds formed between the magnesium ions and lone pairs on surrounding water molecules.

- Hexaaquamagnesium ions are formed,  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ .



- Ions of this sort are acidic.

### ALUMINIUM CHLORIDE, $\text{AlCl}_3$

- At room temperature, solid aluminium chloride has an ionic lattice with a lot of covalent character.
- At temperatures around  $180 - 190^\circ\text{C}$  (depending on the pressure), aluminium chloride converts to molecular form,  $\text{Al}_2\text{Cl}_6$ . This causes it to melt or vaporise because there are now only comparatively weak intermolecular attractions.



- As the temperature increases a bit more, it increasingly breaks up into simple  $\text{AlCl}_3$  molecules.
- Solid aluminium chloride does not conduct electricity at room temperature because the ions are not free to move. Molten aluminium chloride (only possible at increased pressures) does not conduct electricity because still there are no ions.
- The reaction of aluminium chloride with water is surprising. If you drop water onto solid aluminium chloride, you get a violent reaction producing clouds of steamy fumes of hydrogen chloride gas.
- The aluminium chloride reacts with the water rather than just dissolving in it. In the first instance hexaaquaaluminium ions are formed together with chloride ions.



This is very similar to the magnesium chloride equation. The only real difference is the charge on the ion.

### SILICON TETRACHLORIDE, $\text{SiCl}_4$

- Silicon tetrachloride is a simple covalent chloride. There is not enough electronegativity difference between the silicon and the chlorine to form ionic bonds.
- Silicon tetrachloride is a colourless liquid at room temperature which fumes in moist air. The only attractions between the molecules are van der Waals dispersion forces.
- It does not conduct electricity because of the lack of ions or mobile electrons.
- It fumes in moist air because it reacts with water in the air to produce hydrogen chloride.
  - ✓ If water is added to silicon tetrachloride, there is a violent reaction to produce silicon dioxide and fumes of hydrogen chloride.
  - ✓ In a large excess of water, the silicon tetrachloride will dissolve to give a strongly acidic solution containing hydrochloric acid.



### THE PHOSPHORUS CHLORIDES

There are two phosphorus chlorides - phosphorus(III) chloride,  $\text{PCl}_3$ , and phosphorus(V) chloride,  $\text{PCl}_5$ .

#### PHOSPHORUS(III) CHLORIDE (PHOSPHORUS TRICHLORIDE), $\text{PCl}_3$

- This is a simple covalent chloride.
- It becomes a fuming liquid at room temperature.
- Phosphorus trichloride is a liquid because there are only van der Waals dispersion forces and dipole-dipole attractions between the molecules.
- It does not conduct electricity because of the lack of ions or mobile electrons.

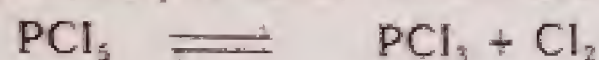


- Phosphorus(III) chloride reacts violently with water to give  $\text{H}_3\text{PO}_3$  and fumes of hydrogen chloride. If lots of water is used then a solution containing hydrochloric acid is formed.



### PHOSPHORUS(V) CHLORIDE (PHOSPHORUS PENTACHLORIDE), $\text{PCl}_5$

- Unfortunately, phosphorus(V) chloride is structurally more complicated.
- Phosphorus(V) chloride is a white solid which sublimes at  $163^\circ\text{C}$ .
- The higher the temperature goes above that, the more the phosphorus(V) chloride dissociates (splits up reversibly) to give phosphorus(III) chloride and chlorine.



- Solid phosphorus(V) chloride contains ions that is why it is a solid at room temperature. The formation of the ions involves two molecules of  $\text{PCl}_5$ .
- Phosphorus(V) chloride has a violent reaction with water producing fumes of hydrogen chloride. As with the other covalent chlorides, if there is enough water present, these will dissolve to give a solution containing hydrochloric acid.
- The reaction occurs in two stages. In the first, with cold water, phosphorus oxychloride,  $\text{POCl}_3$ , is produced along with  $\text{HCl}$ .



- If the water is boiling, the phosphorus(V) chloride reacts further to give phosphoric(V) acid and more  $\text{HCl}$ . Phosphoric(V) acid is also known just as phosphoric acid or as orthophosphoric acid.

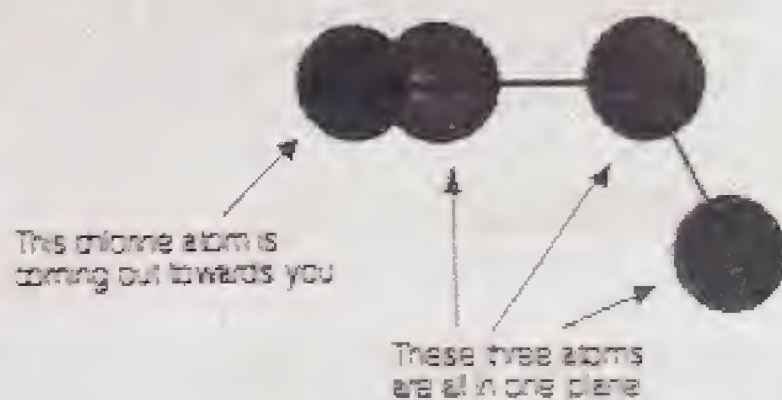


- The overall equation in boiling water is just a combination of these:



### DISULPHUR DICHLORIDE, $\text{S}_2\text{Cl}_2$

- Disulphur dichloride is formed when chlorine reacts with hot sulphur.
- Disulphur dichloride is a simple covalent liquid (orange and smelly).
- The shape is difficult to draw convincingly. The atoms are all joined up in a line but twisted:
- The reason for drawing the shape is to give a hint about what sort of intermolecular attractions are possible. There is no plane of symmetry in the molecule and that means that it will have an overall permanent dipole.
- Disulphur Dichloride has van der Waals dispersion forces and dipole-dipole attractions.
- There are no ions in disulphur dichloride and no mobile electrons, so it never conducts electricity.
- Disulphur dichloride reacts slowly with water to produce a complex mixture of things including hydrochloric acid, sulphur, hydrogen sulphide and various sulphur containing acids and anions.



## QUICK QUIZ-4

1. Which of the following give acidic solution in water:  $\text{MgCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{SiCl}_4$ ,  $\text{NaCl}$

- $\text{MgCl}_2$  and  $\text{NaCl}$  are salts of strong acids and strong bases. So, they do not react with water. Their solution is neutral.

- In a large excess of water,  $\text{SiCl}_4$  will dissolve to give a strongly acidic solution containing hydrochloric acid.



- $\text{AlCl}_3$  is a salt of strong acid and weak base. It reacts with water to produce acidic solution



Salt + water

Base      Acid



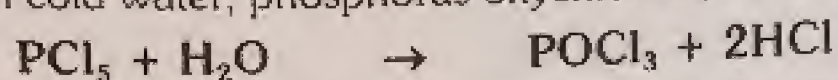
**2. Why NaCl has high melting and boiling point**

Sodium chloride is an ionic solid in which ions are held together by strong ionic bonds. So, lots of energy is needed to break these strong forces. Thus, it has high melting and boiling points.

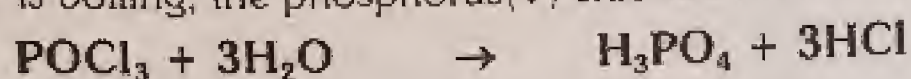
**3. Write equations for reactions of  $\text{PCl}_5$  with hot and cold water.**

The reaction occurs in two stages.

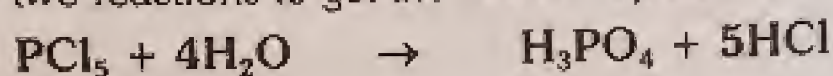
In the first, with cold water, phosphorus oxychloride,  $\text{POCl}_3$ , is produced along with HCl.



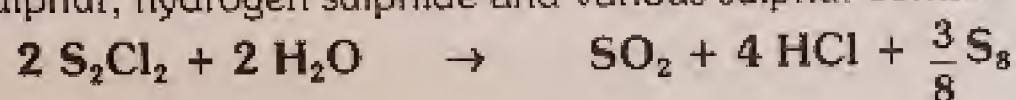
If the water is boiling, the phosphorus(V) chloride reacts further to give phosphoric(V) acid and more HCl.



Add the above two reactions to get the overall equation.

**4. What products are obtained on reaction of disulphide dichloride with water.**

Disulphur dichloride reacts slowly with water to produce a complex mixture of things including hydrochloric acid, sulphur, hydrogen sulphide and various sulphur containing acids and anions.

**5. Why  $\text{AlCl}_3$  is non-conductor in solid as well as in liquid state but  $\text{NaCl}$  and  $\text{MgCl}_2$  are conductor in liquid state and non-conductor in solid state.**

- $\text{NaCl}$  and  $\text{MgCl}_2$  do not conduct electricity in the solid state. It is because they do not have any mobile electrons and the ions free to move. However, they undergo electrolysis when the ions become free on melting.
- Solid aluminium chloride does not conduct electricity at room temperature because the ions are not free to move. Molten aluminium chloride also does not conduct electricity because still there are no free ions.

**HYDROXIDES OF THE PERIOD 3 ELEMENTS****SODIUM AND MAGNESIUM HYDROXIDES**

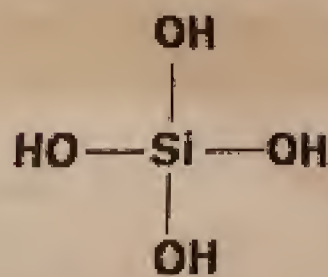
- These contain hydroxide ions, and are simple basic hydroxides.

**ALUMINIUM HYDROXIDE**

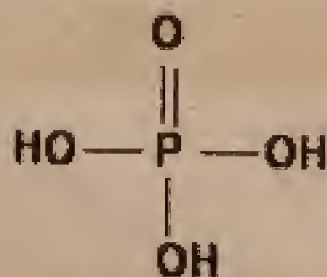
- Aluminium hydroxide, like aluminium oxide, is amphoteric. Thus, it has both basic and acidic properties.

**THE OTHER "HYDROXIDES"**

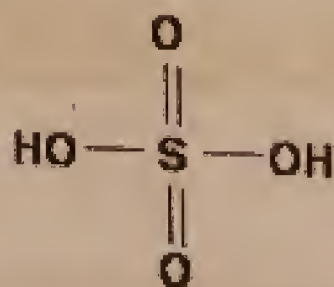
- In all of these have -OH groups covalently bound to the atom from period 3.
- These compounds are all acidic. These range from the very weakly acidic silicic acids to the very strong sulphuric or chloric acids.
- There are other acids (also containing -OH groups) formed by these elements, but these are the ones where the Period 3 element is in its highest oxidation state.



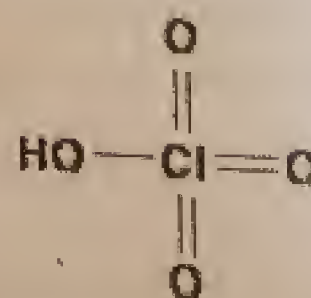
orthosilicic acid



phosphoric(V) acid



sulphuric acid

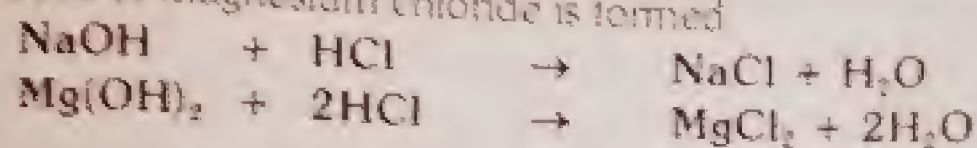


chloric(VII) acid

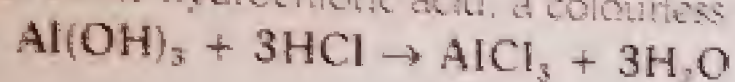


**SODIUM AND MAGNESIUM HYDROXIDES**

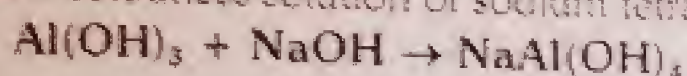
- These are both basic because they contain hydroxide ions which is a strong base.
- Both react with acids to form salts. e.g. with dilute hydrochloric acid, a colourless solution of sodium chloride or magnesium chloride is formed.

**ALUMINIUM HYDROXIDE**

- Aluminium hydroxide is amphoteric.
- Like sodium or magnesium hydroxides, it will react with acids. This is showing the basic side of its nature. With dilute hydrochloric acid, a colourless solution of aluminium chloride is formed.



- But aluminium hydroxide also has an acidic side to its nature. It will react with sodium hydroxide solution to give a colourless solution of sodium tetrahydroxoaluminate.

**THE OTHER "HYDROXIDES"**

- Orthosilicic acid is very weak.
- Phosphoric(V) acid is a weak acid - although somewhat stronger than simple organic acids like ethanoic acid.
- Sulphuric acid and chloric(VII) acids are both very strong acids.
- The main factor in determining the strength of the acid is how stable the anion (the negative ion) is after the hydrogen has been removed. This in turn depends on how much the negative charge can be spread around the rest of the ion.
- If the negative charge stays entirely on the oxygen atom left behind from the -OH group, it will be very attracted to hydrogen ions. The lost hydrogen ion will be easily recaptured and the acid will be weak.
- On the other hand, if the charge can be spread out (delocalised) over the whole of the anion, it will be so spread that it won't attract the hydrogen back very easily. The acid will then be strong.

**QUICK QUIZ-5****1. Which factor determines the strength of acid**

Two factors are responsible for the strength of acids

**(i) Ease of donation of proton. Bond Energy**

Greater the ease of donation of proton, higher is the acidity. This factor mainly depends on the bond energy. Thus, higher the bond energy, lesser is the ability to donate proton and hence lesser is the acidity. e.g. The acidity order among halogen acids is  $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ . The bond energy order is the reverse of this.

**(ii) Stability of the anion (conjugate base)**

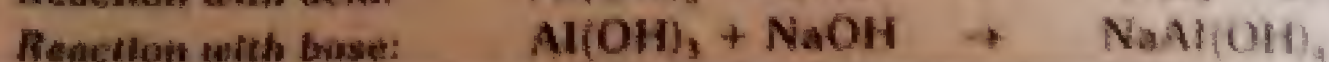
Greater the stability of anion, higher is the acidity. A strong electron withdrawing group can stabilize the anion by attracting electrons of anion towards itself. e.g.



In this, the anion ( $\text{ClO}_4^-$ ) is stabilized by strong electron withdrawing effect of Cl and O. Chlorine and oxygen are highly electronegative elements. Thus,  $\text{HClO}_4$  is the strongest known acid.

**2. Justify that  $\text{Al(OH)}_3$  is amphoteric compound.**

$\text{Al(OH)}_3$  reacts with both acids and bases to form salts. So, it is an amphoteric compound.





# ATOMIC AND PHYSICAL PROPERTIES OF THE GROUP 1 ELEMENTS

Table: Some Physical Properties of alkali metals

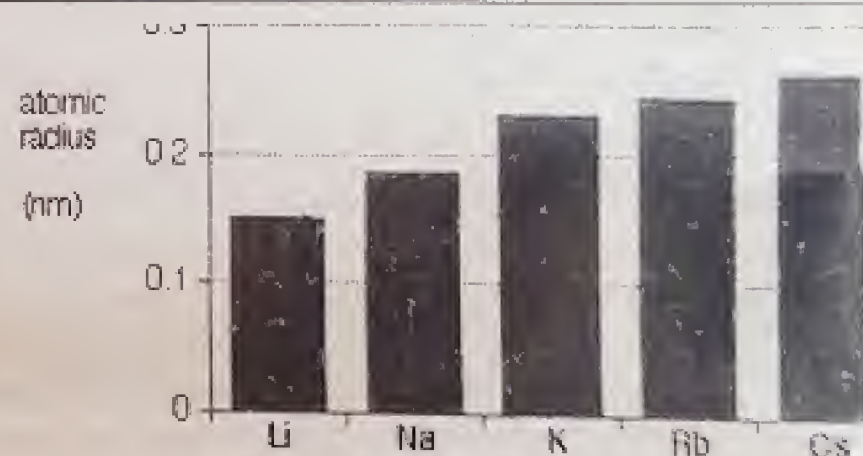
Property	Li	Na	K	Rb	Cs
Atomic weight	6.94	22.99	39.1	85.47	132.91
Atomic volume	12.97	23.63	45.36	55.8	67.3
Atomic (metallic radius for coordination number 12)	1.55	1.9	2.35	2.46	2.6
covalent radius	1.23	1.54	2.03	2.16	2.38
Ionic radius of M <sup>+</sup> ions	0.6	0.95	1.33	1.48	1.69
Melting point	180.5	97.8	63.7	38.9	28.7
Boiling point	1330	892	760	688	670
Ionization energies (kJ/mol) (I <sub>1</sub> )	520.3	495.8	418.9	403.0	375.7
I <sub>2</sub>	7298.1	4562.4	3051.4	2633.0	2238.7
Standard oxidation potential	3.04	2.71	2.99	2.99	2.99
Sublimation energy (eV/ion)	1.7472	1.2432	1.032	0.984	0.9024
Hydration energy (eV/ion)	5.904	3.792	3.6955	3.36	3.624
Electronegativity	1	0.9	0.8	0.8	0.7
Colour of the flame	Crimson red	Golden yellow	Violet	Violet	Violet
Heat of atomisation at 25C (eV/atm)	1.7472	1.2432	1.032	0.984	0.9024
Ionic conduction of M <sup>+</sup> ion	33.5	43.5	64.6	67.5	63

**Shielding Effect or Screening Effect:** The decrease in attraction between outermost electrons and the nucleus due to inner shells electrons is called Shielding effect or screening effect.

## TRENDS IN ATOMIC RADIUS

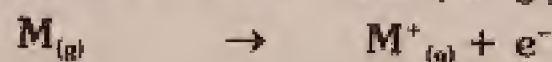
The distance of outermost electron from the nucleus of an atom while considering it spherical is called atomic radius.

**The atomic radius increases down the group from lithium to caesium.** It is because, down the group number of shells increases. So, the atomic volume increases. Moreover, the shielding effect of inner electrons also increases. Hence, atomic and ionic radii (of M<sup>+</sup> ions) increases from lithium to caesium.



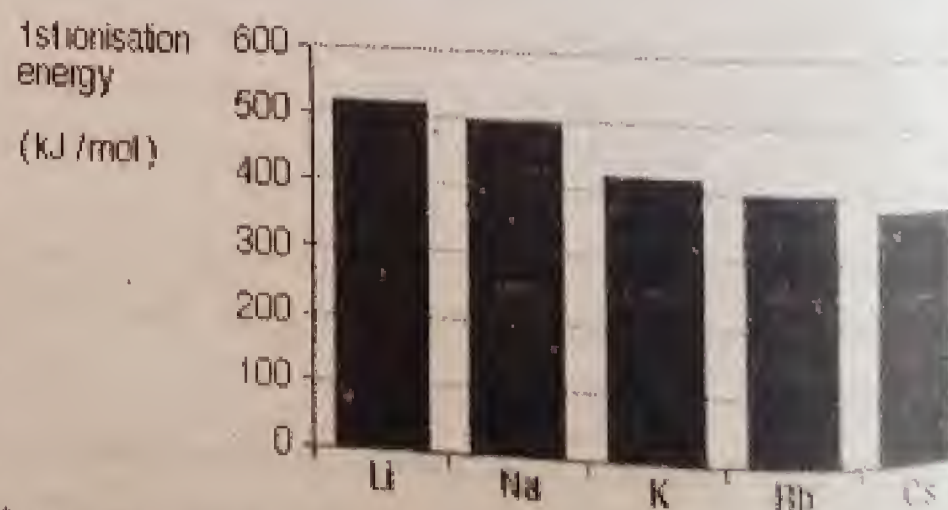
## TRENDS IN FIRST IONIZATION ENERGY

First ionization energy is the energy needed to remove the most loosely held electron from each of one mole of gaseous atoms to make one mole of singly charged gaseous ions.



**The first ionization energy decreases down the group.**

- The alkali metals have only one electron in their outermost shell (ns<sup>1</sup> electron). This ns<sup>1</sup> electron is weakly held with the nucleus. Thus, it can be removed very easily. Therefore, Alkali metals have low ionization energies.
- The distance of ns<sup>1</sup> electron from the nucleus increases from Li to Cs due to increase in atomic size. Thus, its removal becomes more and more easy and the amount of energy required for the removal of ns<sup>1</sup> electron also decreases. Hence, ionization energies of alkali metals decrease from Li to Cs.
- The second ionization energies are fairly high, since the loss of the second electron from M<sup>+</sup> cation. It is because M<sup>+</sup> ion has a noble gas configuration.

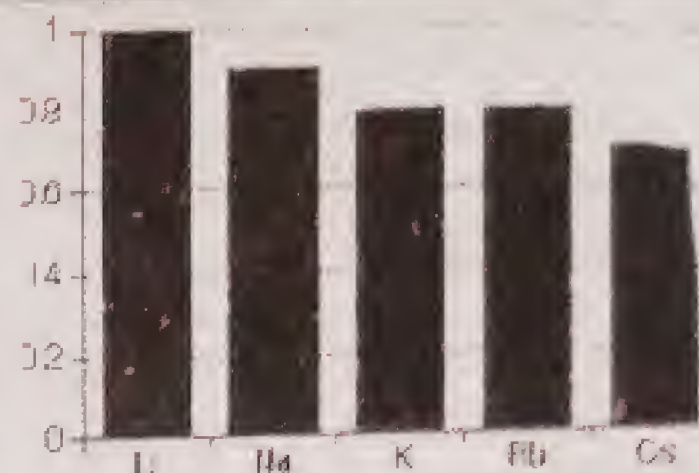




## TRENDS IN ELECTRONEGATIVITY

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons.

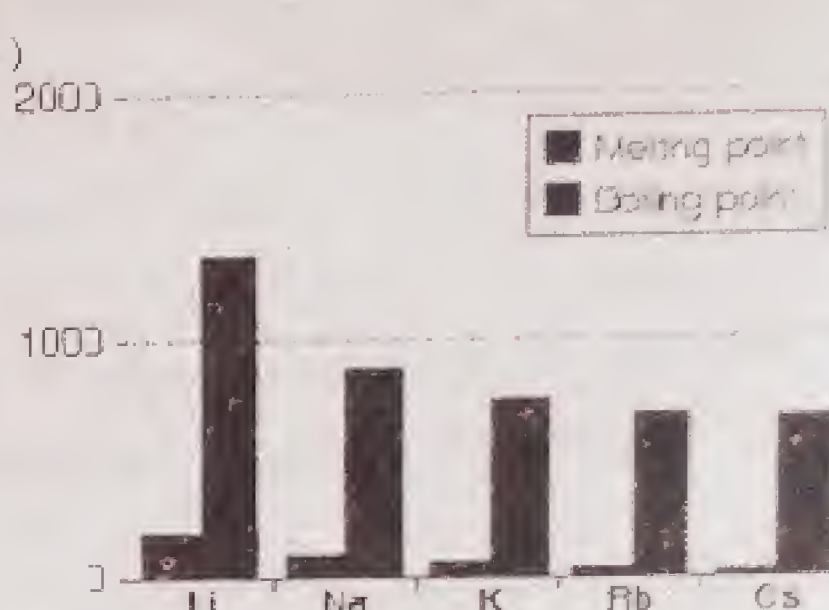
- It is usually measured on the Pauling scale, on which the most electronegative element (fluorine) is given an electronegativity of 4.0.
- It has no unit.
- The electronegativity values decreases down the group from Li to Cs due to increase in atomic size.



## TRENDS IN MELTING AND BOILING POINTS

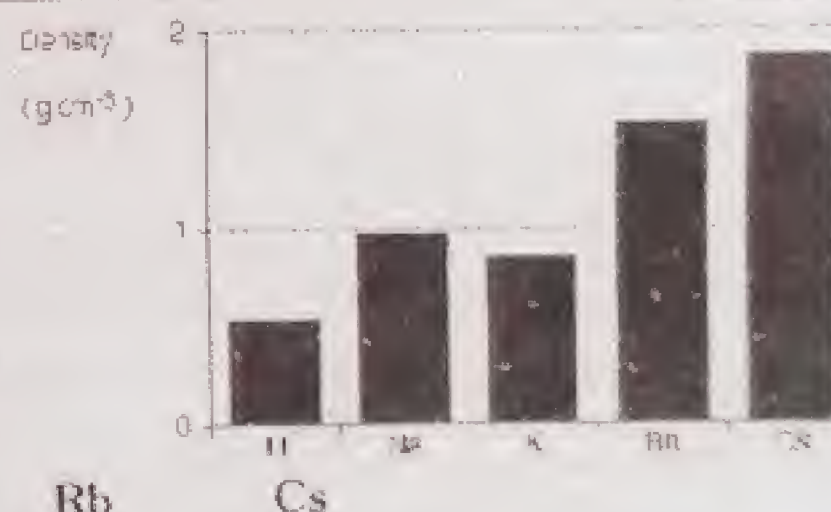
Both the melting points and boiling points decrease down the Group.

- The melting and boiling points are very low due to the presence of weak inter-atomic bonds in the solid state of the alkali metals.
- The bonds are weak due to their larger atomic radii and mainly due to a single valence electron as compared to large number of available vacant orbital.
- As the size of the metal atoms increases, the repulsion of the non-bonding electrons also increases. This increase in the repulsion of non-bonding electron decreases the melting and boiling points of alkali metals from Li to Cs.



## TRENDS IN DENSITY

- The densities of alkali metals are quite low due to the large atomic volumes as shown in the figure.
- Li, Na and K are lighter than water.
- The densities increase with the increase in atomic mass from Li to Cs. It is because increase in atomic mass is more than the increase in atomic volume. So, the density increases.
- K is however, lighter than Na. It is due to an unusual increase in atomic volume of K.



Elements	Li	Na	K	Rb	Cs
Densities at 0°C (g/c.c)	0.534	0.972	0.859	1.525	1.903

## QUICK QUIZ-6

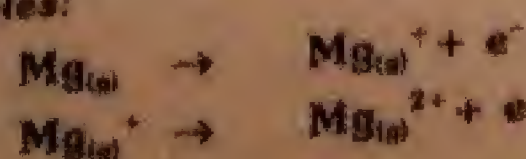
1. Different element imparts different colours in flame?

In certain metals the outer electron is loosely held with the nucleus. So, it can be easily excited to the higher energy levels even by absorbing a small amount of energy in a flame. When this excited electron comes back to its original position, it gives out absorbed energy in the form of light in the visible region. Thus flame appears coloured. The amount of energy absorbed during the excitation process is different in different atoms. Thus different colours are imparted by the atoms to the flame.

2. Explain that 2<sup>nd</sup> ionization energy is greater than 1<sup>st</sup> ionization energy

It is because, due to removal of first electron, hold of the nucleus on the remaining electrons increases. Hence second electron is difficult to remove and thus ionization energy increases

Examples:



$$\Delta H = + 738 \text{ kJ/mole}$$

$$\Delta H = + 1451 \text{ kJ/mole}$$

(1<sup>st</sup> ionization energy)

(2<sup>nd</sup> ionization energy)



3. Why melting point of alkali metals are low as compared to alkaline earth metals.  
It is due to two reasons

- The atomic radii of alkaline earth metals are smaller than those of alkali metals in the same period. Thus, the alkaline earth metals have relatively tight packing of atoms. So, they are harder and have higher melting points than alkali metals.
- Alkali metals have one valence electron. Thus they provide one electron per atom for binding. Alkaline earth metals provide two electrons per atom for binding. So, they have stronger binding forces and have higher melting points than alkali metals.

## CHEMICAL PROPERTIES OF THE GROUP 1 ELEMENTS

### REACTIONS WITH WATER

- With the exception of Li, the alkali metals are extremely soft and readily fused.
- They are highly malleable (i.e. can be pressed out into sheets) and ductile (i.e. can be drawn into wires).
- When freshly cut, they have a bright lustre.
- They are quickly tarnished as soon as metal comes in contact with atmosphere.
- The reactivity of Group 1 metals increases down the Group.

#### Enthalpy changes for the reactions

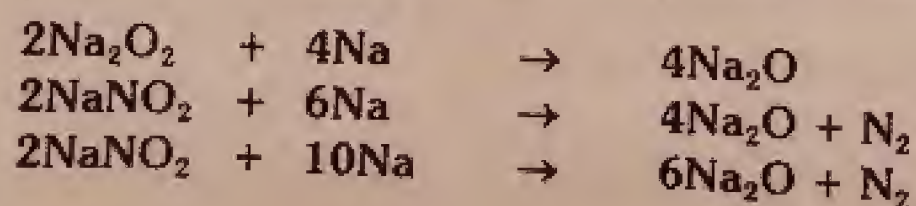
- Generally, enthalpy of reaction increases from Li to Cs.  
$$M_{(s)} + H_2O_{(l)} \rightarrow MOH_{(aq)} + \frac{1}{2} H_{2(g)}$$
- However, there is no regular pattern in these values. They are all fairly similar.
- Lithium releases the most heat during the reaction.
- In each case, metal atoms in a solid form are reacted and metal ions are formed in the solution.
- Overall, what happens to the metal is this:



	Enthalpy change (kJ / mol)
Li	-222
Na	-184
K	-196
Rb	-195
Cs	-203

### REACTIONS WITH OXYGEN

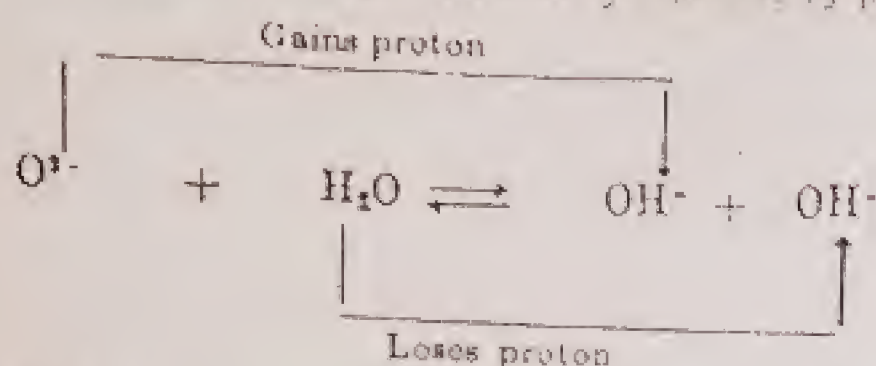
- Alkali metals react with  $O_2$  or air rapidly and thus get tarnished due to the formation of their oxide on the surface of the metals. That is why alkali metals are stored in kerosene or paraffin oil.
- Li when burnt in  $O_2$  gives mainly lithium monoxide, (normal oxide)  $Li_2O$ .  
$$4Li + O_2 \rightarrow 2Li_2O$$
- Na when burnt in  $O_2$  forms sodium peroxide,  $Na_2O_2$   
$$2Na + O_2 \rightarrow Na_2O_2$$
- Other alkali metals react with  $O_2$  to form super oxide of  $MO_2$  type.  
$$M + O_2 \rightarrow MO_2$$
- Normal oxides of alkali metals are not formed by the direct reaction between the metals and  $O_2$  except  $Li_2O$ . They are formed by indirect methods, e.g. by reducing peroxides, nitrite and nitrates with the metal itself.



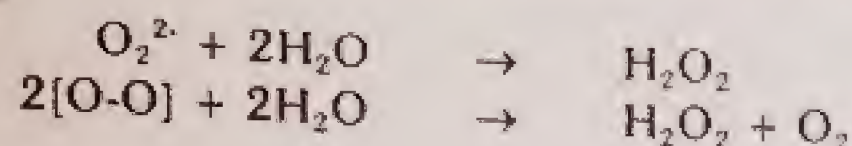


**Properties.**

- Normal oxides ( $O^{2-}$ ) react with  $H_2O$  to form hydroxides by proton exchange.



- The peroxides ( $O_2^{2-}$ ) and superoxides ( $O_2^-$ ) are strong oxidizing agents. These react with  $H_2O$  to give  $H_2O_2$  and  $O_2$ .



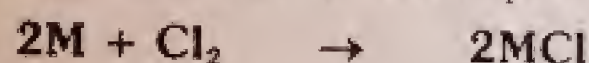
- Normal oxides have anti-fluorite structure. They are ionic in nature since they contain monoxide ion,  $O^{2-}$ .
- Peroxides contain peroxide ion,  $O_2^{2-}$  or  $[-O-O]^{2-}$ .
- The super oxide ion has a three electron bond as shown below.



- The presence of one unpaired electron in it makes this in paramagnetic and coloured.

**REACTIONS WITH CHLORINE**

- Sodium burns with an intense orange flame in chlorine in the same way as it does in pure oxygen.
- The rest also behave the same in both cases.
- In each case, a white solid is produced which is the simple chloride,  $MCl$ .



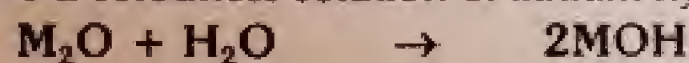
**CHEMICAL PROPERTIES OF THE COMPOUNDS OF GROUP 1 ELEMENTS**

**REACTIONS OF THE OXIDES WITH WATER AND DILUTE ACIDS**

**(i) THE SIMPLE OXIDES,  $X_2O$**

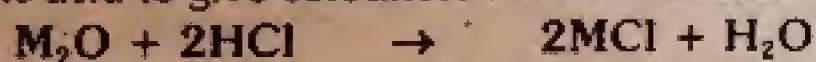
Reaction with water

These are simple basic oxides, reacting with water to give the metal hydroxide. e.g. Lithium oxide reacts with water to give a colourless solution of lithium hydroxide.



Reaction with dilute acids

These simple oxides all react with an acid to give a salt and water. e.g., sodium oxide will react with dilute hydrochloric acid to give colourless sodium chloride solution and water.



**(ii) THE PEROXIDES,  $X_2O_2$**

Reaction with water

- If the reaction is done ice cold then a solution of the metal hydroxide and hydrogen peroxide is formed. These reactions are strongly exothermic. However, during reaction the temperature is controlled so that it does not rise.



- If the temperature increases, the hydrogen peroxide produced decomposes into water and oxygen. The reaction can be very violent overall.
- The temperature rise is generally certain. However, it can be controlled by adding the peroxide very slowly to water.



Reaction with dilute acids

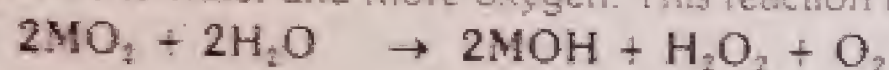
- These reactions are even more exothermic than the ones with water.
- A solution containing a salt and hydrogen peroxide is formed.
- The hydrogen peroxide will decompose to give water and oxygen if the temperature rises again. It is almost impossible to avoid this. This is also a violent reaction.



**III THE SUPEROXIDES,  $XO_2$**

Reaction with water

- This time, a solution of the metal hydroxide and hydrogen peroxide is formed, but oxygen gas is given off as well.
- These are strongly exothermic reactions. Thus, the heat produced will finally decompose the hydrogen peroxide to water and more oxygen. This reaction is also violent.



Reaction with dilute acids

- These reactions are more exothermic than with water. These are also violent reactions.
- A solution containing a salt and hydrogen peroxide is formed together with oxygen gas.
- The hydrogen peroxide will again decompose to give water and oxygen as the temperature rises.



**EFFECT OF HEAT ON NITRATES, CARBONATES AND HYDROGEN-CARBONATES**

**(I) THE FACTS**

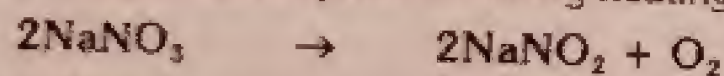
Group 1 compounds are more stable to heat than the corresponding compounds in Group 2.

The lithium compounds behave similarly to Group 2 compounds.

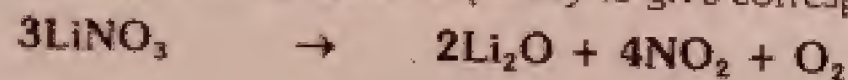
The rest of Group 1 behave similarly but in a different way than Group 2.

Nature of carbonates, bicarbonates and nitrates

- The carbonates ( $M_2CO_3$ ) and bicarbonates ( $MHCO_3$ ) are highly stable to heat.
- With increase of electropositive character from Li to Cs, the stability of these salts increases.
- Their nitrates decompose on strong heating to the corresponding nitrite and  $O_2$ .



- The  $LiNO_3$  decomposes completely to give corresponding oxide,  $NO_2$  and  $O_2$ .



**QUICK QUIZ-7**

**(II) EXPLAINING THE TREND IN TERMS OF THE POLARISING ABILITY OF THE POSITIVE ION**

1. Why lithium salts are more covalent in nature while salts of other alkali metals are ionic.

When cations approach near an anion, they attract the outer most electrons of the anion and repels the nucleus. Thus the distortion or polarization of the anion takes place. This distortion results in the sharing of electrons between two oppositely charged ions. So, a bond between the cation and anion becomes partly covalent in character. In general the smaller cations polarize the anions more effectively than bigger one. Therefore, the lithium salts are slightly covalent while other alkali metal salts are ionic.

2. Give trend of stability of carbonates of alkali and alkaline earth metals along group.

- The solubility of alkali metal carbonates increases down the group due to increase in ionic character.
- Generally, the solubility of alkaline earth metal carbonates decreases down the group except  $BaCO_3$  which has slightly more solubility than  $SrCO_3$ . So, a clean trend is not found.



3. Show bonding in superoxide ion.

- The super oxide ion has a three electron bond as shown below



- The presence of one unpaired electron in it makes this ion paramagnetic and coloured.

4. Why alkali metals stores in kerosene or paraffin oil.

Alkali metals react with  $\text{O}_2$  or air rapidly and thus get tarnished due to the formation of their oxide on the surface of the metals. They also react very fast with water vapours present in the air. That is why alkali metals are stored in kerosene or paraffin oil to prevent these reactions.

## FLAME TESTS

- Flame tests are used to identify the presence of a relatively small number of metal ions in a compound.
- All metal ions do not give flame colours.
- Flame tests is the easiest way of identifying metals in the compounds of Group I elements.
- For other metals, there are usually other easy methods available which are more reliable.

## PROCEDURE FOR FLAME TEST

- Take a platinum or nichrome (a nickel-chromium alloy) wire.
- Clean it by dipping it into concentrated hydrochloric acid and then holding it in a hot Bunsen flame.
- Repeat this until the wire does not produce any colour in the flame.
- Moisten the clean wire with some of the acid and then dip it into a small amount of the solid. Some solid sticks to the wire.
- Place the wire back in the flame again.
- If the flame colour is weak, then dip the wire back in the acid again and put it back into the flame.
- A very short but intense flash of colour is obtained.
- Different colours are shown by different elements as shown in table.

## RESULT: THE COLOURS

Different colours shown by different elements as shown in table

How to differentiate between different red colours obtained in flame test?

- Get samples of known lithium, strontium (etc.) compounds.
- Repeat the flame test with known and unknown compounds.
- Comparing the colour produced by known compounds and the unknown compound side by side until a good match is obtained.

FLAME COLOUR	
Li	red
Na	golden yellow
K	lilac (pink)
Rb	red (reddish violet)
Cs	blue
Ca	orange red
Sr	red
Ba	pale green
Cu	blue green (often with white flashes)
Pb	greyish white

## THE ORIGIN OF FLAME COLOURS

- In alkali metal atoms the outer  $ns^1$  electron is loosely held with the nucleus. So, it can be easily excited to the higher energy levels even by a small amount of heat energy (e.g. by heating the metals or their salts into Bunsen burner).



- During the excitation process the electron absorbs some energy. When this excited electron comes back to its original position, it gives out absorbed energy in the form of light in visible region of the electromagnetic radiations.
- The amount of energy absorbed during the excitation process is different in different atoms. Thus, different colours are imparted by the atoms to the flame.
- The property of alkali metals to give colouration in the burner flame has been used to detect their presence in salts. This test is known as the flame test.

## QUICK QUIZ-8

(1) **Ion of which element among the alkali metals has the greatest polarizing power?**

In general, the smaller cations polarize the anions more effectively than bigger one. Therefore, the lithium ion has the greatest polarizing power.

(2) **Justify the placing of Li, Na, K, Rb, and Cs in the same group of the periodic table.**

The valence shell electronic configuration of Li is  $2s^1$  which is in accordance with that of other alkali metals ( $ns^1$ ). Thus, due to similar electronic configuration, Li shows similar chemical properties. Hence it is placed in alkali metals group.

(3) **Write the electronic configuration for alkali metal atoms.**

Element	Electronic Configuration	Short configuration
Li	$1s^2 2s^1$	$[\text{He}] 2s^1$
Na	$1s^2 2s^2 2p^6 3s^1$	$[\text{Ne}] 3s^1$
K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	$[\text{Ar}] 4s^1$
Rb	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$	$[\text{Kr}] 5s^1$
Cs	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1$	$[\text{Xe}] 6s^1$
Fr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^1$	$[\text{Rn}] 7s^1$

(4) **Explain the periodicity in ionization energy, electronegativity and atomic radii on passing from Li to Rb.**

- Atomic radii increases from Li to Rb due to increase in number of shells and shielding effect.
- Ionization energy decreases from Li to Rb due to increase in size
- Electronegativity decreases from Li to Rb due to increase in size

(5) **Among alkali metals atoms which has the largest ionization potential?**

Lithium (Li) metal has highest ionization energy due to its smallest size among alkali metals.

(6) **Explain the following:**

(a) **Alkali metals show an oxidation state +1 only**

Alkali metals have only one valence electron which is easily lost due to low first ionization energy. After the loss of one electron, they get the noble gas configuration. So, it becomes highly difficult to remove second electron from them. Therefore, they have high second ionization energy. Hence they do not show oxidation state greater than +1.

(b) **Alkali metals are univalent.**

Alkali metals have only one valence electron which is easily lost due to low first ionization energy. After the loss of one electron, they get the noble gas configuration. So, it becomes highly difficult to remove second electron from them. Therefore, they have high second ionization energy. Hence they are univalent.

(c) **alkali metals are good reducing agents**

Alkali metals have low ionization energy. So, they can easily loose electrons i.e. they are easily oxidized. Thus they can reduce substances and act as excellent reducing agents.

(d) **alkali metals have low m.pts**

Alkali metals have only one valence electron. So, they provide only one electron for binding. Therefore, they have weaker binding forces and hence they have low melting points.



e) Alkali metals give characteristic colour to the Bunsen flame.

In alkali metals, the outer electron ( $ns^1$ ) is loosely held with the nucleus. So, it can be easily excited to the higher energy levels even by absorbing a small amount of energy in a flame. When this excited electron comes back to its original position, it gives out absorbed energy in the form of light in the visible region. Thus Bunsen flame appears coloured. e.g. Na gives golden yellow colour, K gives lilac (pink) colour.

f) Na is stored under kerosene.

Na reacts with  $O_2$  or air rapidly and thus gets tarnished due to the formation of oxide on its surface. It also reacts very fast with water vapours in the air. To prevent these reactions, Na is stored under kerosene or paraffin oil.

g) alkali metal form  $M^+$  cations instead of  $M^{2+}$  cations

Alkali metals have only one valence electron which is easily lost due to low first ionization energy. After the loss of one electron, they get the noble gas configuration. So, it becomes highly difficult to remove second electron from them. Thus, they have high second ionization energy. Hence they form  $M^+$  ions instead of  $M^{2+}$  ions.

h) Alkali metals have low ionization potentials.

Alkali metals have larger size than other atoms in the same period. So, their outermost electron is loosely held with the nucleus and can be removed easily. Hence, they have low ionization potentials.

(7) Hydroxides of 1<sup>st</sup> group are strong bases. Explain why?

Since, alkali metal ions are larger in size, therefore, their bases have low lattice energies. So, they completely ionize in water, dissolve and produce high concentration of  $OH^-$  ions. Hence, hydroxides of 1<sup>st</sup> group are strong bases.

(8) Explain the following:

$Li_2CO_3$  is unstable while other alkali metal carbonates are relatively more stable.

Smaller ions have high charge density.  $Li^+$  ion being smaller has high charge density, so it attracts  $O^{2-}$  ions from polarized carbonate ion effectively. Thus,  $Li_2CO_3$  is decomposed on heating.



Moreover, due to small size of  $Li^+$  and  $O^{2-}$  ions, their packing becomes tight in the crystal. Thus strong electrostatic forces are developed in  $Li_2O$  and it becomes stable. Hence,  $Li_2O$  is formed readily on heating  $Li_2CO_3$ .

## GROUP 2 ELEMENTS

### ATOMIC AND PHYSICAL PROPERTIES

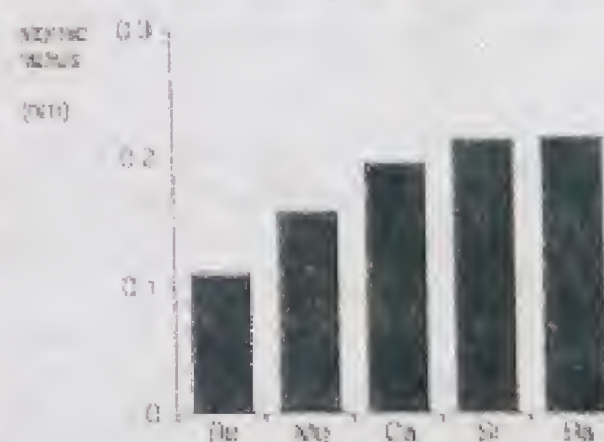
The Group 2 elements are: beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr) and barium (Ba).

### TRENDS IN ATOMIC RADIUS

- The figure shows the Atomic Radii of the Group 2 elements.
- Beryllium is particularly a small atom compared with the rest of the Group.
- The atomic radius increases down the group from Be to Ra. It is because, down the group number of shells increases. So, the atomic volume increases. Hence, atomic and ionic radii (of  $M^{2+}$  ions) increases from Be to Ra.
- The atomic radii of these elements are however, smaller than those of alkali metals in the same period. It is because the alkaline earth metals have higher nuclear charge which pulls the electrons more towards the nucleus.
- Due to smaller atomic radii, the alkaline earth metals are harder, have higher densities and higher melting points than alkali metals.

The Table gives some physical properties of alkaline earth metals.

Atomic Radii of the Group 2 elements





Property	Be	Mg	Ca	Sr	Ba	Ra
Atomic weight	9.01	24.31	40.08	87.62	137.34	226
Abundance (% of earth's crust)	6.4 x 10.4	2.0	3.45	0.915	0.040	1.3x10.10
Density (gm/c.c.)	1.84	1.74	1.55	2.54	3.75	6.00
Melting point (°C)	1277	650	838	763	714	700
Boiling point (°C)	2770	1107	1440	1380	1610	--
Atomic volume (c.c.)	4.90	13.97	25.9	34.54	36.7	38.0
Atomic (i.e., metallic) radius for co-ordination number 12 (Å°)	1.12	1.60	1.97	2.15	2.22	--
Covalent radius (Å°)	0.90	1.36	1.74	1.91	1.98	--
Tonic (crystal radius of M <sup>2+</sup> ion for co-ordination number + (Å°)	0.31	0.65	0.99	1.13	1.35	1.40
Ionisation energies (KJ/mole)						
I <sub>1</sub>	899.5	737.7	829.8	547.5	502.9	509.4
I <sub>2</sub>	1757.1	1450.7	1145.4	1064.3	965.2	979.06
I <sub>1</sub> + I <sub>2</sub>	2656.6	2188.4	1735.2	1613.8	1468.1	1488.46
Oxidation state	+2	+2	+2	+2	+2	+2
Electronegativity	1.5	1.2	1.0	0.9	0.9	0.9
Flame colouration	None	None	Brick red	Crimson	Apple green	Red
Oxidation potentials (volts) for M (s) → M <sup>2+</sup> (aq) + 2e <sup>-</sup>	1.70 1.70	1.37	2.87	2.89	2.90	2.92
Heat of atomisation at 25°C and 1 atm pressure (KJ/mole)	327.26	146.89	181.21	163.21	175.77	--
Heat of hydration (KJ/mole)	2385.45	1925.1	1653.07	1458.67	1276.42	--
Ionic potential of M <sup>2+</sup> ion (i.e., charge/radius ratio).	6.66	3.08	2.12	1.82	1.55	1.33

### TRENDS IN FIRST IONIZATION ENERGY

First ionization energy is the energy needed to remove the most loosely held electron from each of one mole of gaseous atoms to make one mole of singly charged gaseous ions.

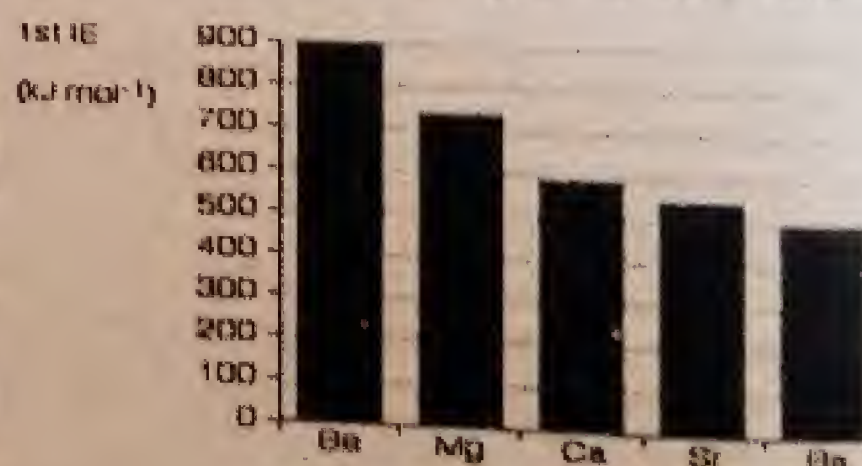


- The figure shows the first ionization energy of the Group 2 elements
- The first and second ionization energies of these elements decrease with the increase of atomic radii from Be to Ba.

It is because, the distance of outer electrons from the nucleus increases from Be to Ra due to increase in atomic size. So, removal of electrons becomes more and more easy and thus amount of energy required for the removal electrons also decreases. Hence, ionization energies decreases from Be to Ra.

- Ra has slightly higher first and second ionization energies than Ba.

First Ionisation Energy of the Group 2 elements



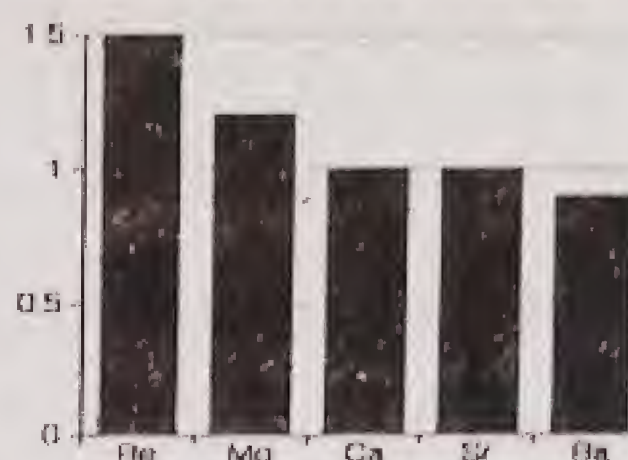


## TRENDS IN ELECTRONEGATIVITY

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons.

- It is usually measured on the Pauling scale, on which the most electronegative element (fluorine) is given an electronegativity of 4.0.
- It has no unit.
- The figure shows the electronegativities of the Group 2 elements.
- The electronegativity values increases down the group.**
- It is due to following reasons.
  - Down the group atomic size increases. Thus, the distance of bonding pair increases from the metal nucleus. Hence, bonding pairs are less strongly attracted and so, the electronegativity decreases.
  - Moreover, the bonds formed between these metals and other things (e.g. chlorine) become more and more ionic down the group. Thus, the bonding pair is pulled away from the Group 2 element towards the other things (e.g. chlorine).

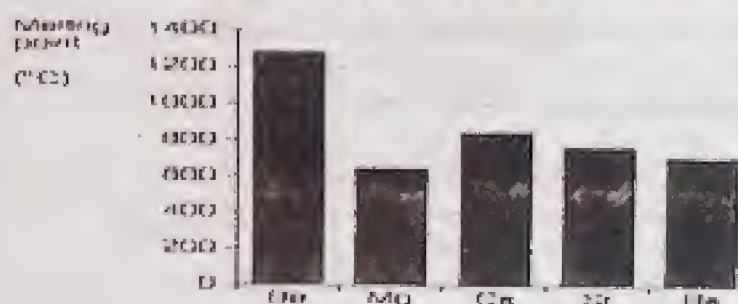
Electronegativity of the Group 2 elements



## TRENDS IN MELTING POINT AND BOILING POINT

- The melting and boiling points of Group 2 elements are higher than Group 1 elements.** It is because Group 2 elements have two valence electrons. So, they form greater number of bonds than Group 1 elements.
- Generally, no regular trend is present in the melting and boiling points of Group 2 elements.

Melting Points of the Group 2 elements



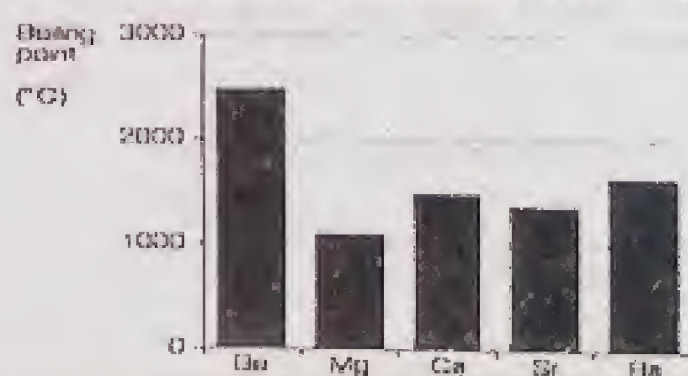
### Melting points

The figure shows that the melting point decreases down the Group. However, the smooth decreasing trend is broken by magnesium.

### Boiling points

The figure shows that there is no regular pattern in boiling points.

Boiling Points of the Group 2 elements



## CHEMICAL PROPERTIES OF THE ELEMENTS OF GROUP 2 ELEMENTS

### REACTIONS WITH WATER

**The reactivity increases down the group.** It is because, down the group ability to give electrons increases.

### THE FACTS

#### Beryllium

Beryllium has no reaction with water or steam even at red heat.

#### Magnesium

- Magnesium burns in steam to produce white magnesium oxide and hydrogen gas.



- Very clean magnesium ribbon has a very slight reaction with cold water. After several minutes, some bubbles of hydrogen form on its surface. The coil of magnesium ribbon usually floats to the surface.
- However, the reaction soon stops because the magnesium hydroxide formed is almost insoluble in water and forms a barrier on the magnesium preventing further reaction.



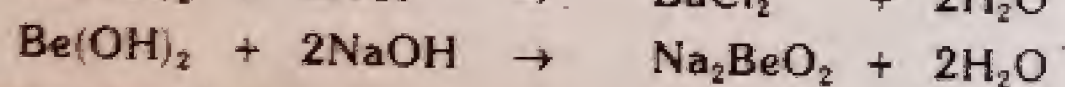


## Calcium, Strontium and Barium

- These all react with cold water to give the metal hydroxide and hydrogen.
- Strontium and barium have reactivities similar to lithium in Group 1 of the Periodic Table.
- Calcium reacts fairly vigorously with cold water. The reaction is exothermic. The bubbles of hydrogen gas are given off, and a white precipitate (of calcium hydroxide) is formed, and solution becomes alkaline. The solution becomes alkaline due to calcium hydroxide which is slightly soluble.
- The equation for the reactions of any of these metals would be:
 
$$M_{(s)} + 2H_2O_{(l)} \rightarrow M(OH)_{2(aq \text{ or } s)} + H_{2(g)}$$
- The solubility of hydroxides increases down the Group.
- The calcium hydroxide forms mainly as a white precipitate because it only slightly dissolves in water. However, down the group less precipitates are formed because solubility of hydroxide increases down the group.
- The Group 2 metals become more reactive towards water as you go down the Group.

## TREND IN REACTIVITY

- $Be(OH)_2$  is not at all basic. It is amphoteric since it reacts with acids to form salts and with alkalis to give beryllates.



- The hydroxides of other metals are basic in nature.
- **The basic character increases on moving down the group.** Thus  $Mg(OH)_2$  is weakly basic while  $Ba(OH)_2$  is the strongest base. It is because with the increase in size of  $M^{2+}$  cation, both the polarity of  $M-OH$  bond and the internuclear distance between oxygen of  $OH^-$  ion and the metals atom increase. Thus, there is greater ionization of  $M(OH)_2$  and hence basic character increases.
- Due to high polarising power of small  $Be^{2+}$  in  $Be(OH)_2$ , it is covalent. All other hydroxides are ionic.
- The solubility of hydroxides increases down the Group as shown by the solubility products.
 

$Be(OH)_2 = 1.6 \times 10^{-26}$	$Mg(OH)_2 = 8.9 \times 10^{-12}$	
$Ca(OH)_2 = 1.3 \times 10^{-4}$	$Sr(OH)_2 = 3.2 \times 10^{-4}$	$Ba(OH)_2 = 5.4 \times 10^{-2}$
- Thus,  $Be(OH)_2$  and  $Mg(OH)_2$  are almost insoluble in  $H_2O$ . The hydroxides of other metals are slightly soluble.

## REACTIONS WITH OXYGEN AND NITROGEN

### (a) FORMATION OF SIMPLE OXIDES

- The alkaline earth metals form the normal oxides of  $MO$  type.
- These are obtained either by heating the metal in  $O_2$  or by heating their carbonates at high temperature



### Properties:

- These oxides are extremely stable white crystal line solids due to their high crystal lattice energy obtained by packing doubly charged in a sodium chloride type of lattice.
- $BeO$  and  $MgO$  are quite insoluble in  $H_2O$  while  $H_2O$ ,  $CaO$ ,  $SrO$  and  $BaO$  react with  $H_2O$  to give soluble hydroxides,  $M(OH)_2$  which are strong bases.
- $BeO$  is not basic in nature. In fact it is amphoteric since it reacts with acids to form salts and with alkalis to give beryllates.

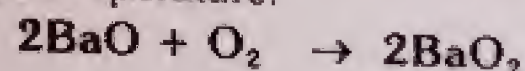




- The oxides of other metals are basic in character. Their basic character increases on moving down the group.
- $\text{Be}^{2+}$  ion has high polarizing power due to small size. Thus,  $\text{BeO}$  is covalent while other oxides are ionic.
- Although  $\text{BeO}$  is covalent yet it has a higher melting point and is harder than the oxides of other metals as it is polymeric.
- Each  $\text{Be}$  atom is tetrahedrally coordinated by four oxygen atoms.

### (b) FORMATION OF PEROXIDES.

- The peroxides of heavier metals ( $\text{Ca}$ ,  $\text{Sr}$ ,  $\text{Ba}$  etc.) can be obtained on heating the normal oxides with  $\text{O}_2$  at high temperature.



#### Properties:

- The peroxides are white, ionic solids having peroxide anion,  $[\text{O}-\text{O}]^{2-}$ .
- They react with acids to produce  $\text{H}_2\text{O}_2$ .

### (c) FORMATION OF NITRIDES ON HEATING IN AIR

- All the elements burn in nitrogen to form nitrides,  $\text{M}_3\text{N}_2$  e.g.



- These react with  $\text{H}_2\text{O}$  to liberate  $\text{NH}_3$ .



- $\text{Be}_3\text{N}_2$  is volatile while other nitrides are not so.

## TRENDS IN SOLUBILITY OF THE HYDROXIDES, SULPHATES AND CARBONATES

### I- SOLUBILITY OF THE HYDROXIDES

The solubility of hydroxides of Group 2 metals increases down the Group.

#### Magnesium hydroxide

It appears to be insoluble in water. However, shake it with water, filter it and test the pH of the solution, it will be slightly alkaline. It shows that there are more hydroxide ions in the solution than pure water. So, some magnesium hydroxide must have dissolved.

#### Calcium hydroxide

Its solution is used as "lime water". One litre of pure water will dissolve about 1 gram of calcium hydroxide at room temperature.

#### Barium hydroxide

It is soluble enough and produce a solution with a concentration of around  $0.1 \text{ mol dm}^{-3}$  at room temperature.

### II- SOLUBILITY OF THE SULPHATES

The solubility of sulphates of Group 2 metals decreases down the Group.

### III- SOLUBILITY OF THE CARBONATES

- The solubility of carbonates of Group 2 metals decreases down the Group.
- Carbonates are insoluble in water and therefore occur as solid rock minerals in nature.
- However they dissolve in  $\text{H}_2\text{O}$  containing  $\text{CO}_2$  due to the formation of bicarbonates.





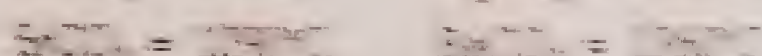
## THE EFFECT OF HEAT ON THE GROUP 2 CARBONATES AND NITRATES

### THE EFFECT OF HEAT ON THE GROUP 2 CARBONATES

- All carbonates decompose on heating to give the metal oxide and  $\text{CO}_2$ .



- The order of the decomposition temperatures of these carbonates is given below:



- As you go down the group, the decomposition temperature of carbonates increases down the group, hence the stability increases.
- The stability of carbonates of Group 2 metals increases down the Group.

### THE EFFECT OF HEAT ON THE GROUP 2 NITRATES

- All nitrates of Group 2 metals undergo thermal decomposition to give the metal oxide, nitrogen dioxide and oxygen.

- The nitrates are white solids, and the oxides produced are also white solids. Brown nitrogen dioxide gas is given off together with oxygen.



- When heated, the nitrates initially lose water of crystallisation. So, the solid may become anhydrous before it starts to decompose.
- The stability of nitrates of Group 2 metals increases down the Group.

#### Summary

- The stability of both carbonates and nitrates increases down the Group.
- Thus the carbonates and nitrates of lower metals need to be heated more strongly to decompose than those at the top.

## HOW BERYLLIUM DIFFERS FROM OTHER MEMBERS OF ITS GROUP?

### Exercise Q 1 (a) In How Beryllium differs from other members of its group?

Beryllium, the first element of the group, differs from rest of alkaline earth metals due to following reasons:

(i) small atomic size

(ii) comparatively high electronegativity.

The main points of difference are:

- Fluorescence:** Beryllium is the faintest of all the elements of its group.
- Melting and boiling points:** The melting and boiling points of beryllium are the highest.
- Formation of covalent compounds:** Beryllium has a tendency to form covalent compounds. Thus when it reacts with other elements the electronegativity difference is not so large and the bond is therefore covalent.
- Reaction with water:** Beryllium does not react with water even at high temperature. Other alkaline earth metals decompose water liberating  $\text{H}_2$  gas.
- Reaction with hydrogen:** Beryllium does not react with hydrogen directly to form its hydride. Its hydride has been prepared indirectly. The rest of the alkaline earth metals combine with hydrogen to form hydrides. The hydrides of Be and Mg are covalent, whereas the hydrides of other metals are ionic.
- Reaction with alkalis:** Beryllium reacts with alkalis to form hydrogen.



Other alkaline earth metals do not react with alkalis.



7. **Behaviour of oxides and hydroxides:** The oxides and hydroxides of beryllium are amphoteric, i.e. dissolve in both acids and alkalis to form salts.



8. **Behaviour of carbides:** Beryllium carbide is decomposed by water to form methane ( $\text{CH}_4$ ).



The carbide of other alkaline earth metals are decomposed by water to form acetylene ( $\text{C}_2\text{H}_2$ ). For example:



9. **Behaviour of nitrides:**  $\text{Be}_3\text{N}_2$  is volatile while the nitrides of other alkaline earth metals are non-volatile.

10. **Number of molecules of water of crystallisation:** The salts of  $\text{Be}^{2+}$  ion cannot have more than four molecules of water of crystallisation while other alkaline earth metals have more than four molecules of water of crystallisation. It is because, in case of  $\text{Be}^{2+}$  ion there are only four orbitals. One orbital can accept only one lone pairs of electrons denoted by O-atoms of the water molecules as shown below.

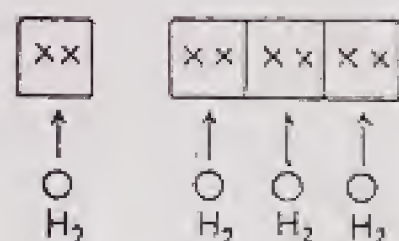
Valence-shell  
electronic configuration  
of Be atom ( $2s^2, 2p^0$ ) }



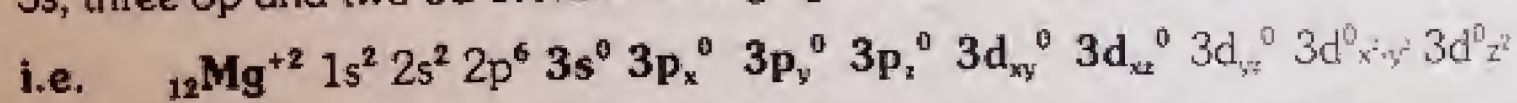
Valence-shell configura-  
tion of  $\text{Be}^{2+}$  ion ( $2s^0, 2p^0$ ) }



Attachment of  $4\text{H}_2\text{O}$  mole-  
cules with  $\text{Be}^{2+}$  ion }



On the other hand, other alkaline earth metals like Mg can extend their coordination number to six by using one 3s, three 3p and two 3d orbitals belonging to their outermost shell. Thus, Mg in  $\text{Mg}^{+2}$  state is



11. **Formation of complex compounds:**  $\text{Be}^{2+}$  ion, on account of its small size, forms stable complex compounds like  $[\text{BeF}_3]^-$ ,  $[\text{BeF}_4]^{2-}$ . The  $\text{M}^{2+}$  ions derived from other alkaline earth metals form very few complex compounds.

## QUICK QUIZ-9

(1) Among the alkaline earth metals atoms which has the highest ionization potential?

Be has the smallest size among alkaline earth metals so it has the highest ionization potential.

(2) Explain why Ca, Sr, Ba, and Ra are placed in one group of the periodic table.

The general valence shell electronic configuration of all these elements is  $ns^2$ . Thus, due to similar electronic configuration these elements show similar chemical properties. Hence these are placed in same group.

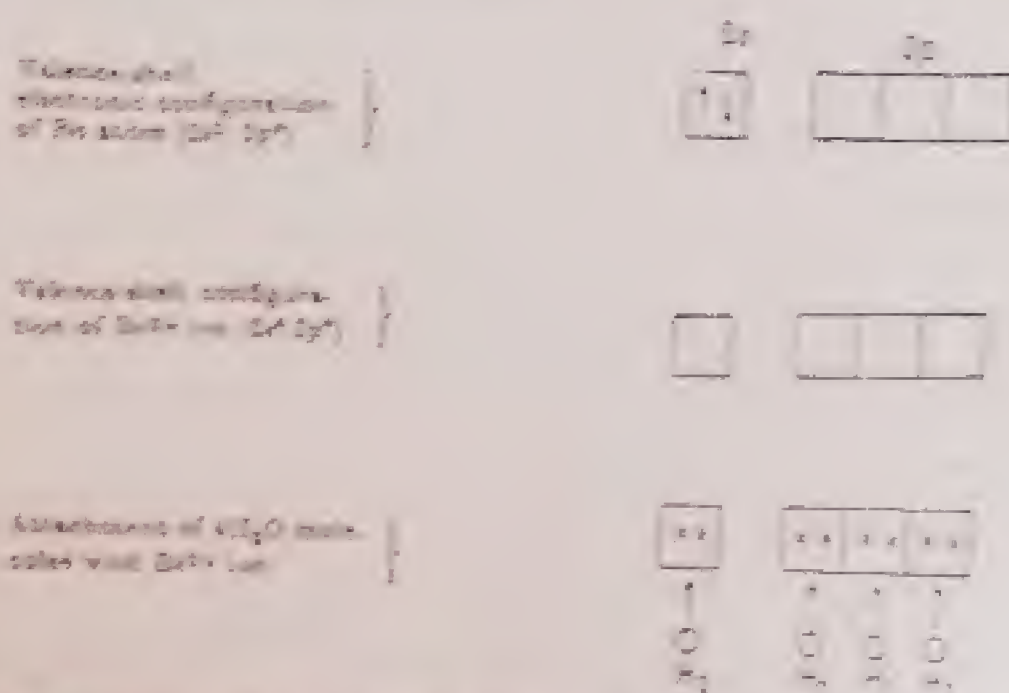
(3) Explain the following

(a) Alkaline earth metals form  $\text{M}^{2+}$  ions but no  $\text{M}^+$  ions.

Alkaline earth metals have two valence electrons. Both these electrons have quite low ionization energies. So, both these electrons are lost easily. Hence they form  $\text{M}^{2+}$  ions instead of  $\text{M}^+$  ions.



- (b) Although the value of 2<sup>nd</sup> ionization potential of alkaline earth metals is higher than that of 1<sup>st</sup> ionization potential yet these metals form  $M^{2+}$  ions instead of  $M^+$  ion.  
It is because, by the removal of both electrons, the alkaline earth metals get the configuration of noble gases. Hence, they form  $M^{2+}$  ions instead of  $M^+$  ion.
- (c) Beryllium salts have never more than four molecules of water of crystallisation.  
In case of  $Be^{2+}$  ion there are only four orbitals, namely, one orbital can accept lone pairs of electrons donated by O-atoms on each of the water molecules as shown below:



On the other hand, other alkaline earth metals like Mg can extend their coordination number to six by using one 3s, three 3p and two 3d orbitals belonging to their outermost shell.

- (d) The solubility of the sulphates of alkaline earth metals decreases whereas the solubility of their hydroxides increases on moving down the group.
- In hydroxides,  $OH^-$  is a small anion. So, lattice energy depends upon the size of cations of alkaline earth metals only. Here, lattice energy overcomes the hydration energy. The size of cations increases down the group, so, the lattice energy decreases and therefore the solubility of hydroxides increases.
  - In sulphates,  $SO_4^{2-}$  ion is common, which is a quite bigger anion. Hence, hydration energy overcomes the lattice energy. So down the group, hydration energy decreases due to increase in the size of cations of alkaline earth metals, thus, solubility of sulphates decreases down the group.
- (e) The thermal stability of carbonates of alkaline earth metals increases in atomic numbers.  
It is because, in small size ions the gain in electrostatic attraction while converting to oxide is considerable. In case of large cation, the gain in electrostatic attraction is relatively much less and the decomposition is difficult. Since the size of cation increases down the group, therefore, stability also increases.
- (f) Alkaline earth metals salts impart colour to the Bunsen flame.  
In alkaline earth metals, the outer electron is loosely held with the nucleus. So, it can be easily excited to the higher energy levels by absorbing a small amount of heat energy. When this excited electron comes back to its original position, it gives out absorbed energy in the form of light in visible region. Different amount of energy is absorbed in different atoms for excitation of electron. Thus, different colours are imparted by the atoms to the flame.
- (g)  $MgSO_4$  is more soluble in water than  $BaSO_4$ .  
It is because, the  $SO_4^{2-}$  ion is common in both. This ion is a quite bigger anion. Hence, hydration energy overcomes the lattice energy. Since, size of  $Ba^{2+}$  ion is greater than that of  $Mg^{2+}$  ion so hydration energy of  $Ba^{2+}$  ion is less than  $Mg^{2+}$  ion.
- (h) Alkaline earth metals form  $M^{2+}$  ions but not  $M^{3+}$  ions.
- It is because, alkaline earth metals have two valence electrons. By the removal of both electrons, the alkaline earth metals get the configuration of noble gases and thus they form  $M^{2+}$  ions.
  - It becomes very difficult to remove the third electron from a noble gas configuration ion. Therefore, 3<sup>rd</sup> ionization energy of alkaline earth metals is quit high. Hence, they cannot form  $M^{3+}$  ions.



How do the elements of group IIA differ from alkali metals

See Page 57 for the difference

The hydroxides of group IIA metals are weaker than those of group IA metals.

Group IIA metals have smaller size than group IA metals. Due to smaller size, the packing of their ions is quite tight in their crystal lattice. Moreover, the cations of group II metals are divalent ( $M^{2+}$ ) which show more attractions for hydroxide anions. So, they have high lattice energies. Hence, their ionization is lesser and therefore, they are weaker base than those of group IA metals.

The carbonates of group IIA metals are less stable to heat than those of group IA metals.

It is because, small size ions have high polarizing power. In small size ions the gain in electrostatic attraction while converting to oxide is considerable. In case of large cation, the gain in electrostatic attraction is relatively much less and the decomposition is difficult. Since, alkaline earth metals have smaller size, therefore, their carbonates are less stable because they are decomposed easily.

KOH is stronger base than  $Ba(OH)_2$ .

KOH is completely dissociated in water thus giving higher concentration of  $OH^-$  ions than that of  $Ba(OH)_2$ .

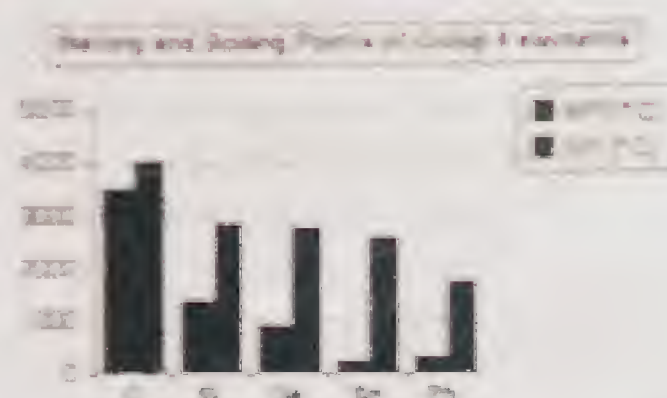
## GROUP 4 ELEMENTS

The Group 4 elements are carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb).

## ATOMIC AND PHYSICAL PROPERTIES OF THE ELEMENTS

### MELTING POINTS AND BOILING POINTS

- The figure shows the melting and boiling Points of Group 4 elements.
- The melting points and boiling points generally decrease down the group. However, the decrease is not regular.
- The decrease in melting and boiling points shows that inter-atomic forces also decrease down the group. The melting and boiling points of C and Si are very high. It is because both of these elements form giant molecules.
- The melting point of tin is less than lead. It is due to forming a distorted 1,2-co-ordinated structure rather than a pure one. The tin values in the figure are for metallic white tin.



### BRITTLENESS

If a substance shatters when force is applied then this property is called brittleness.

- Carbon as diamond is very hard. It shows the strength of the covalent bonds. However, if it is hit with a hammer, it shatters. Thus, it is brittle.
- Silicon, germanium and grey tin have same structures as diamond. They are also brittle solids.
- However, white tin and lead have metallic structures. The atoms can slip over each other without breaking of the metallic bonds. Thus, these have typical metallic properties like being malleable and ductile.
- Lead in particular is a fairly soft metal.

### ELECTRICAL CONDUCTIVITY

- Carbon as diamond does not conduct electricity. In diamond the electrons are all tightly bound and not free to move.
- Silicon, germanium and grey tin are semiconductors.
- White tin and lead are normal metallic conductors of electricity.
- Thus, electrical conductivity increases down the group from typically non-metallic conductivity (benzene) of carbon as diamond to the typically metallic behaviour of white tin and lead.

### ELECTRONEGATIVITY

- Carbon is the most electronegative elements of this group.
- The electronegativities decrease with increase of atomic number. However, this increase is not regular. The irregularity is due to the filling of the d-orbital in case of Ge and Sn and f-orbitals in case of Pb.



## IONIZATION ENERGIES

The ionization energy values decrease down the group from C to Pb. However, the decrease is not regular.

The irregularity is due to the filling of the d-orbitals in case of Ge and Sn and f-orbitals in case of Pb. Since d and f-orbitals have poor shielding effect, so they cannot shield the valence electron effectively. Hence, the pattern becomes irregular.

**Remember!**

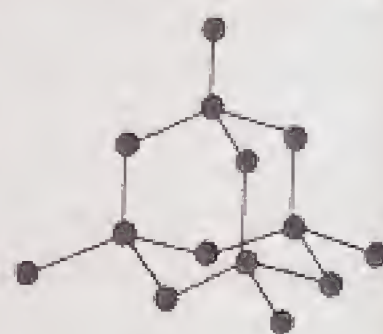
The similar explanation can be given for irregularities in atomic radii, electronegativity etc.

## THE TREND FROM NON-METAL TO METAL IN THE GROUP 4 ELEMENTS

### STRUCTURES OF THE ELEMENTS

The metallic character increases down the group in Group 4 elements.

- Carbon at the top of the Group has giant covalent structures. It has two common allotropes, diamond and graphite.
- Diamond has a three-dimensional structure of carbon atoms each joined covalently to four (4) other atoms as shown in the figure.
- This same structure is found in silicon and germanium and in one of the allotropes of tin, which is "grey tin" or "alpha-tin".
- The common allotrope of tin ("white tin" or "beta-tin") is metallic. In this form atoms are held together by metallic bonds. Its structure is a distorted close-packed arrangement. In close-packing, each atom is surrounded by twelve (12) near-neighbours.
- Thus, a clear trend is found down the group from the typical covalency in non-metals to the metallic bonding in metals.
- The change-over in the two entirely different structures of tin is the exception.



**Exercise Q3 (viii)** Explain the trends in oxidation states with suitable examples.

## OXIDATION STATE

The apparent charge positive or negative on an atom in a substance is called its oxidation state or oxidation number.

### (a) INERT PAIR EFFECT AND POSITIVE OXIDATION STATES

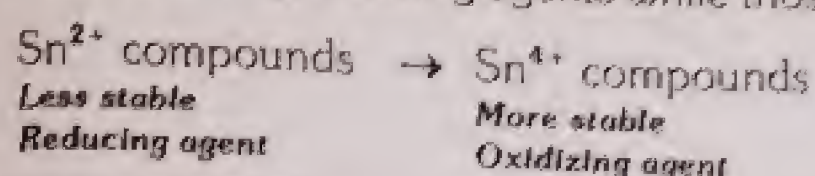
- Carbon and silicon commonly show +4 oxidation states.
  - Germanium commonly shows both +2 and +4 oxidation states.
  - Tin and Pb commonly shows +2 oxidation states.
  - When two  $np^2$  electrons are lost from the  $ns^2np^2$  configuration, the elements show +2 oxidation states.
  - The two electrons in  $ns^2$  are not lost in the formation of  $M^{2+}$  cations. This pair of  $ns^2$  electrons is called inert pair of electrons.
  - The stability of +2 oxidation state increases from  $Ge^{2+}$  to  $Pb^{2+}$  i.e.  $Ge^{2+} < Sn^{2+} < Pb^{2+}$
  - When all the four  $ns^2np^2$  electrons are lost, the elements show +4 oxidation state, i.e.  $M^{4+}$  cations are formed.
  - The stability of +4 oxidation state decrease down the group. i.e.  $Ge^{4+} > Sn^{4+} > Pb^{4+}$
- Compounds of  $Ge^{2+}$  are less stable than those of  $Ge^{4+}$ . Hence the compounds of  $Ge^{2+}$  are readily changed into those of  $Ge^{4+}$ . Thus, compounds of  $Ge^{2+}$  act as strong reducing agents while those of  $Ge^{4+}$  act as oxidizing agents.

$Ge^{2+}$ compounds	→	$Ge^{4+}$ compounds
Less stable		More stable
Reducing agent		Oxidizing agent

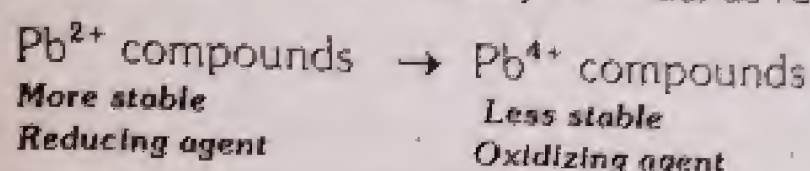
**Remember!** A reducing agent reduces other but is itself oxidized.  
e.g.  $Ge^{2+}$  gives electrons to form  $Ge^{4+}$  (itself oxidized).  
The electrons lost by  $Ge^{2+}$  are added to some other species. So, that species is reduced. Hence,  $Ge^{2+}$  is a reducing agent.



- Similarly, it can be shown that the compounds of  $\text{Sn}^{2+}$  are less stable than those of  $\text{Sn}^{4+}$ . Thus, compounds of  $\text{Sn}^{2+}$  act as strong reducing agents while those of  $\text{Sn}^{4+}$  act as oxidizing agents.



- Similarly,  $\text{Pb}^{2+}$  compounds are more stable than those of  $\text{Pb}^{4+}$ . Thus, compounds of  $\text{Pb}^{4+}$  act as strong oxidizing agents while those of  $\text{Pb}^{2+}$  act as reducing agents.

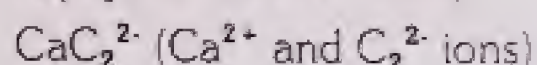
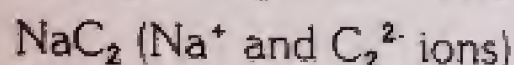
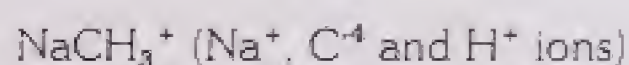
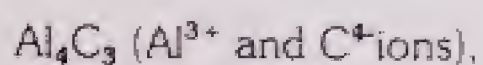
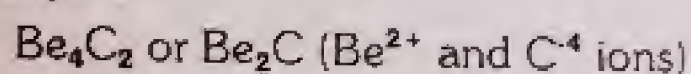


- Thus, the order of stability of  $\text{M}^{2+}$  and  $\text{M}^{4+}$  cations of Ge, Sn and Pb is  
 $\text{Ge}^{2+} < \text{Ge}^{4+}$ ;  $\text{Sn}^{2+} < \text{Sn}^{4+}$ ;  $\text{Pb}^{2+} > \text{Pb}^{4+}$

#### (b) NEGATIVE OXIDATION STATE

- Since the electronegativities of these elements are low, they do not have much tendency to form the negative ion.
- However, carbon forms  $\text{C}^{4-}$  and  $\text{C}_2^{2-}$  ions in certain compounds.

#### Examples:



**Exercise Q3 (ix)** Discuss the inert pair effect in the:

(a) formation of ionic bonds (b) formation of covalent bonds

#### THE INERT PAIR EFFECT IN THE FORMATION OF IONIC BONDS

- If the elements in Group 4 form  $2+$  ions, they will lose the  $p^2$  electrons, leaving the  $s^2$  pair unused.

e.g. to form a lead(II) ion, lead will lose the two  $6p$  electrons, but the  $6s$  electrons will be left unchanged, which is the "inert pair".

- Generally, ionization energies decreases down the group. However, in Group 4, this does not quite happen.

- The total ionization energy needed to form the  $2+$  ions are shown in the figure in  $\text{kJ mol}^{-1}$ . The figure shows there is a slight increase between tin and lead. It shows that it is slightly more difficult to remove the  $p$ -electrons from lead than from tin.

1st+2nd IEs



- The total ionization energy needed to form the  $4+$  ions are shown in the figure in  $\text{kJ mol}^{-1}$ . The difference between tin and lead is more prominent. The relatively large increase between tin and lead must be because the  $6s^2$  pair is significantly more difficult to remove in lead than the corresponding  $5s^2$  pair in tin. It can be explained by Theory of Relativity.

1st+2nd+3rd+4th IEs



#### Relativistic Contraction

With the heavier elements like lead, **relativistic contraction** of the electrons tends to draw the electrons more closer to the nucleus than expected. Thus, they are more difficult to remove. The heavier the element, the greater this effect.

This affects  $s$ -electrons much more than  $p$ -electrons.

In the case of lead, the relativistic contraction makes it more difficult to remove the  $6s$  electrons than expected. The energy releasing in other process like lattice enthalpy and hydration enthalpy are not enough to compensate for this extra energy. It means for lead it is not energetically favourable to form  $4+$  ions.

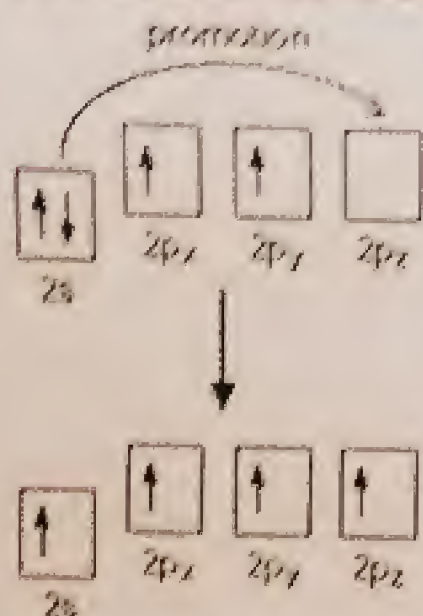


### THE INERT PAIR EFFECT IN THE FORMATION OF COVALENT BONDS

- Consider the case of carbon. It normally forms four covalent bonds rather than two.
- Its electronic configuration is



- There are only two unpaired electrons.
- Before carbon forms bonds, though, it normally promotes one of the s-electrons to the empty p-orbital.



- Thus there becomes 4 unpaired electrons. These undergo hybridization to form 4 covalent bonds.
- The energy for promotion of s-electron is supplied because the carbon can then form twice as many covalent bonds. Each covalent bond formation releases energy which is more than needed for excitation.
- The lead cannot do this. It is because bond energies decreases down the Group due to increasing size. Thus, the bonding pair goes away from the two nuclei and better screened from them.  
e.g., the energy released when two extra Pb-X bonds are formed may no longer be enough to compensate for the extra energy needed to promote a 6s electron into the empty 6p orbital.
- This becomes even more difficult, if the energy gap between the 6s and 6p orbitals was increased by the relativistic contraction of the 6s orbital.

## CHEMICAL PROPERTIES OF THE ELEMENTS OF GROUP 4 ELEMENTS

### THE CHLORIDES OF CARBON, SILICON AND LEAD

#### STRUCTURES AND STABILITY

#### STRUCTURES

#### CARBON, SILICON AND LEAD TETRACHLORIDES

- These all have the formula  $\text{MCl}_4$ .
- They are all simple covalent molecules with a typical tetrahedral shape.
- All of them are liquids at room temperature. However, at room temperature, lead(IV) chloride will tend to decompose to give lead(II) chloride and chlorine gas.

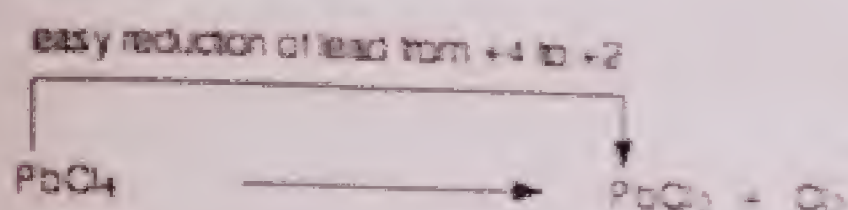
#### Lead(II) chloride, $\text{PbCl}_2$

- It is a white solid.
- Its melting point is  $501^\circ\text{C}$ .
- It is very slightly soluble in cold water, but more soluble in hot water.
- It is mainly ionic in character.



### STABILITY

- The most stable oxidation state shown by Group 4 elements is +4
- This oxidation state is shown by carbon and silicon in  $\text{CCl}_4$  and  $\text{SiCl}_4$ . These therefore have no tendency to split up to give dichlorides.
- However, the relative stability of the +4 oxidation state decreases down the Group while stability of +2 oxidation state increases.
- Lead(IV) chloride decomposes at room temperature to give the more stable lead(II) chloride and chlorine gas.



### REACTION WITH WATER (HYDROLYSIS)

The hydrolysis of tetrahalides takes place through the following two steps

#### Step-I.

- In this step oxygen atoms of  $\text{H}_2\text{O}$  which acts as a donor
- These attacks the central atoms of the halide to form a coordinate bond with it and thus produces an unstable intermediate compounds  $\text{MX}_4 \cdot \text{H}_2\text{O}$

#### Step-II

- In this step four  $\text{HX}$  molecules are eliminated from this unstable intermediate compound and hydroxide of the central element is formed. Thus X atoms of  $\text{MX}_4$  molecule are replaced by  $\text{OH}^-$  ions.

**Tetrahalides of C are not hydrolysed while those of Si, Ge and Sn get readily hydrolysed.**

- The C-atom being a member of 2<sup>nd</sup> period of the periodic table, has no d-orbitals in its valance shell. Thus, it is unable to accommodate the lone pair donated by the donor oxygen atom of  $\text{H}_2\text{O}$  molecule to form an unstable intermediate compounds. Hence, the tetrahalides of C are not hydrolysed.
- On the other hand Si, Ge and Sn have vacant d-orbitals. These can accept the lone pair and thus the tetrahalides get readily hydrolysed.
- Ease of hydrolysis of tetrahalides by  $\text{H}_2\text{O}$  decreases from Si to Sn due to increase in the metallic character of the central atom. Thus  $\text{GeX}_4$  and  $\text{SnX}_4$  tetrahalides are less readily hydrolysed than  $\text{SiX}_4$  tetrahalides.
- It must be noted however, that empty orbitals are always present with any atom. They can be utilized only if sufficient energy is provided for the reaction to occur, e.g.,  $\text{CCl}_4$  undergoes hydrolysis when superheated steam is used.



**Superheated steam** is the steam at a temperature higher than its vaporization (boiling) point at the same pressure.

- Hydrolysis of tetrahalides of Pb follows essentially the same pattern. It is due to the instability of tetravalent compounds of Pb. Some decomposition of  $\text{PbCl}_4$  to  $\text{PbCl}_2$  also takes place



- $\text{PbCl}_4$  is hydrolysed by  $\text{H}_2\text{O}$  as follows:



- The tetrahalides of Si, Ge, Sn and Pb react with halide ions and form the hexahalo complex ions like  $[\text{SiF}_6]^{2-}$ ,  $[\text{GeX}_6]^{2-}$ , e.g.



- The tetrahalides of C are exception. They do not form such complex ions.

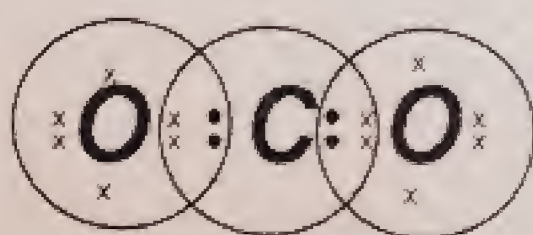


**OXIDES**

- There is a large difference between the physical properties of carbon dioxide and silicon dioxide (also known as silicon(IV) oxide or silica).
- Carbon dioxide is a gas whereas silicon dioxide is a hard high-melting solid.
- The other dioxides in Group 4 are also solids. This is also due to the difference in structure between carbon dioxide and the dioxides of the rest of the Group.

**THE STRUCTURE OF CARBON DIOXIDE**

- The dipole moment of carbon dioxide is zero. Therefore it is a linear molecule.

**THE STRUCTURE OF SILICON DIOXIDE**

- It is a macromolecular compound, in which silicon and oxygen atoms are linked together covalently in tetrahedral basic unit.
- In cristobalite, these units are joined as in diamond, while in quartz and tridymite they are arranged spirally around an axis.
- Due to this structure silicon dioxide is non-volatile and hard unlike carbon dioxide.

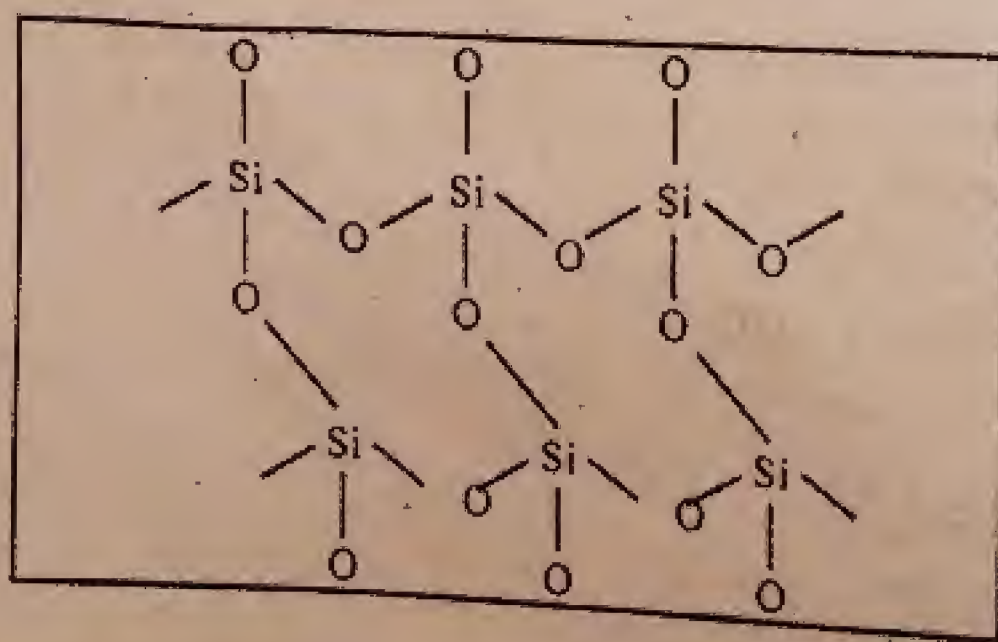
**Similarity between structure of silicon dioxide and carbon dioxide**

- Triatomic molecules of silicon dioxide and carbon dioxide, carbon and silicon are similar in having.
  - (i) 4 valence electrons.
  - (ii) 4 covalent bond formation.

**Differences between structure of silicon dioxide and carbon dioxide**

But they show a lot of difference in their physical properties. It is due to the fact that:

- (i) Silicon atoms are much larger in size than carbon atoms and thus tend to be surrounded by more oxygen atoms.
- (ii) Silicon forms only single bond with oxygen atoms while carbon forms double bonds.
- (iii) Carbon forms a linear molecule of  $\text{CO}_2$  with two oxygen atoms. While silicon atom is bound to four oxygen atoms in a tetrahedral structure which result in the formation of silicon dioxide crystal. The simplest formula for silica is  $\text{SiO}_2$ . However the whole crystal of silicon can be considered as one molecule.





Exercise Q3 (x) Discuss in detail acid-base trend in group 4 oxides

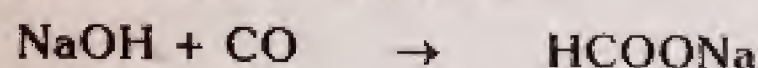
### THE ACID-BASE BEHAVIOUR OF THE GROUP 4 OXIDES

- The oxides of the elements at the top of Group 4 are acidic.
- The acidity of the oxides decreases down the Group.
- Towards the bottom of the Group, the oxides become more basic. However, they do not lose their acidic character completely. Thus they become amphoteric.
- An oxide which can show both acidic and basic properties is said to be **amphoteric**.
- The trend is therefore from acidic oxides at the top of the Group towards amphoteric ones at the bottom.

### CARBON AND SILICON OXIDES

#### CARBON MONOXIDE

- It is treated as if it is a neutral oxide. However, it is very slightly acidic.
- It does not react with water, but it will react with hot concentrated sodium hydroxide solution to give a solution of sodium methanoate.



- This reaction shows that it must be acidic.

#### CARBON AND SILICON DIOXIDES

These are both weakly acidic.

##### Reactions with water

- Silicon dioxide does not react with water. It is due to the difficulty of breaking up the giant covalent structure.
- Carbon dioxide does react with water to a slight extent to produce hydrogen ions (strictly, hydroxonium ions) and hydrogencarbonate ions.



- The solution of carbon dioxide in water is sometimes known as carbonic acid. It is actually about 0.1% of the carbon dioxide has actually reacted. The position of equilibrium is well to the left-hand side.

##### Reactions with bases

- Carbon dioxide reacts with sodium hydroxide solution in the cold to give either sodium carbonate or sodium hydrogencarbonate solution.
- The ratio of both depends upon the relative amounts of reactants.



- Silicon dioxide reacts only with hot and concentrated sodium hydroxide solution. Sodium silicate solution is formed.



- The famous reaction in the blast furnace extraction of iron is also with a basic species, CaO.
  - ✓ In this reaction calcium oxide (from the raw material limestone) reacts with silicon dioxide to produce a liquid slag called calcium silicate.
  - ✓ This reaction also shows the acidic behaviour of silicon dioxide reacting with a base (CaO).



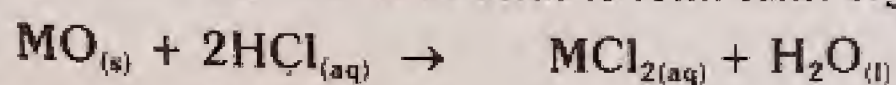


**GERMANIUM, TIN AND LEAD OXIDES****THE MONOXIDES**

All of these oxides are amphoteric (they show both basic and acidic properties).

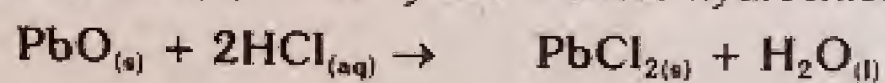
**The basic nature of the oxides**

- These oxides all react with acids to form salts. e.g., they all react with concentrated hydrochloric acid.

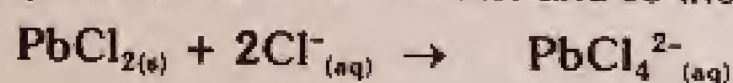


where M can be Ge and Sn. However, lead shows a different behaviour.

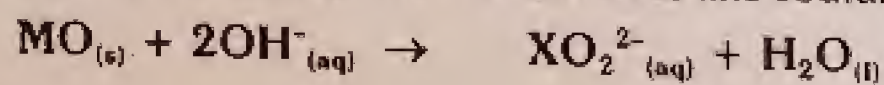
- Lead(II) chloride is fairly insoluble in water and, instead of getting a solution. It will form an insoluble layer over the lead(II) oxide by use of dilute hydrochloric acid. Thus reaction is stopped.



- However, with concentrated hydrochloric acid it does not happen. In concentrated acid, the large excess of chloride ions react with the lead(II) chloride to produce soluble complexes such as  $\text{PbCl}_4^{2-}$ . These ion complexes are soluble in water and so the problem disappears.

**The acidic nature of the oxides**

- All of these oxides also react with bases like sodium hydroxide solution.



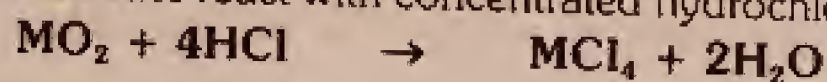
- Lead(II) oxide, for example, would react to give  $\text{PbO}_2^{2-}$  [plumbate(II) ions].

**THE DIOXIDES**

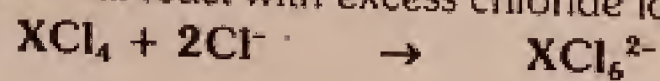
These dioxides are again amphoteric. Thus these shows both basic and acidic properties.

**The basic nature of the dioxides**

- The dioxides react with concentrated hydrochloric acid first to give compounds of the type  $\text{MCl}_4$



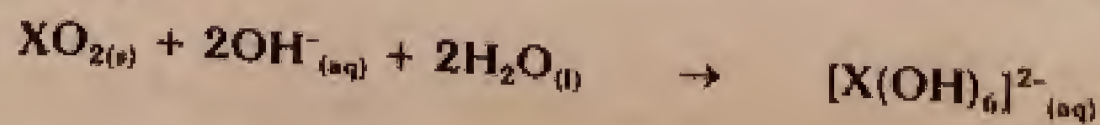
- These will react with excess chloride ions in the hydrochloric acid to give complexes such as  $\text{XCl}_6^{2-}$



- In the case of lead (IV) oxide, the reaction is carried out with ice-cold hydrochloric acid. It is because if the reaction is done any warmer, the lead (IV) chloride decomposes to give lead(II) chloride and chlorine gas. This shows the preferred oxidation state of lead being +2 rather than +4.

**The acidic nature of the dioxides**

- The dioxides will react with hot concentrated sodium hydroxide solution to give soluble complexes of the form  $[\text{M}(\text{OH})_6]^{2-}$ .



- Some sources suggest that the lead(IV) oxide needs molten sodium hydroxide. In that case, the equation is different.





## QUICK QUIZ-10

- Why tin melting point is low as compared to lead**  
The melting point of tin is less than lead. It is due to forming a distorted 1:2 coordinated tetrahedral structure.
- Give trend of conductivity 4<sup>th</sup> group element**  
The electrical conductivity increases down the group from typically non-metallic (insulator) behaviour of carbon as diamond to the typically metallic behaviour of white tin and lead.
- Which of the following metals are semiconductors Pb, C, Si, Ge**  
Si and Ge are semiconductors.
- Arrange follow cations in increasing order of their stability  $\text{Sn}^{+2}$ ,  $\text{Sn}^{+4}$ ,  $\text{Ge}^{+2}$ ,  $\text{Pb}^{+2}$**   
(Most stable)  $\text{Ge}^{+2} > \text{Pb}^{+2} > \text{Sn}^{+4} > \text{Sn}^{+2}$  (Least stable)

## GROUP 7-ELEMENTS: (HALOGENS)

### ATOMIC AND PHYSICAL PROPERTIES

The Group 7 elements (the halogens) are: fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). Astatine is a radioactive substance and its chemistry is not much known.

### TRENDS IN ATOMIC RADIUS

Atomic radius increases down the group due to increase number of shells, greater shielding effect and less nuclear charge.

**Exercise Q3:** (a) Explain in detail the trends in group 7 of following physical properties. (a) Electronegativity (b) Electron affinity

### TRENDS IN ELECTRONEGATIVITY

- Halogens have large values of electronegativity.
- These values decrease down the group from F to I.
- Large electronegativity values of halogen atoms indicate that X atoms (e.g. F) form a strong bond with X<sup>-</sup> ions (e.g. F<sup>-</sup> ions).

Atomic radii of the halogens (pm)



### TRENDS IN FIRST ELECTRON AFFINITY

Electron affinity values decrease from Cl to I.  
However, the electron affinity value of F is less than that of Cl due to its small size.

### TRENDS IN MELTING AND BOILING POINTS

- The melting and boiling points of the halogens regularly increase from F to I.  
It is because, halogens exist as molecules. So, with increase in size, polarity, and mass, the intermolecular forces between molecules becomes stronger.
- $\text{F}_2$  and  $\text{Cl}_2$  are gases at ordinary temperature. Br is a heavy liquid while I is a solid.

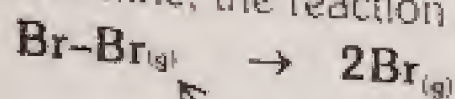
### BOND ENTHALPIES (BOND ENERGIES OR BOND STRENGTHS)

- Bond enthalpy is the heat needed to break one mole of a covalent bond to produce individual atoms, starting from the original substance in the gas state, and ending with gaseous atoms.
- For chlorine,  $\text{Cl}_{2(g)}$ , it is the heat energy needed to carry out the change  $\text{Cl}_{2(g)} \rightarrow 2\text{Cl}_{(g)}$ .





- For bromine, the reaction is still from gaseous bromine molecules to separate gaseous atoms.



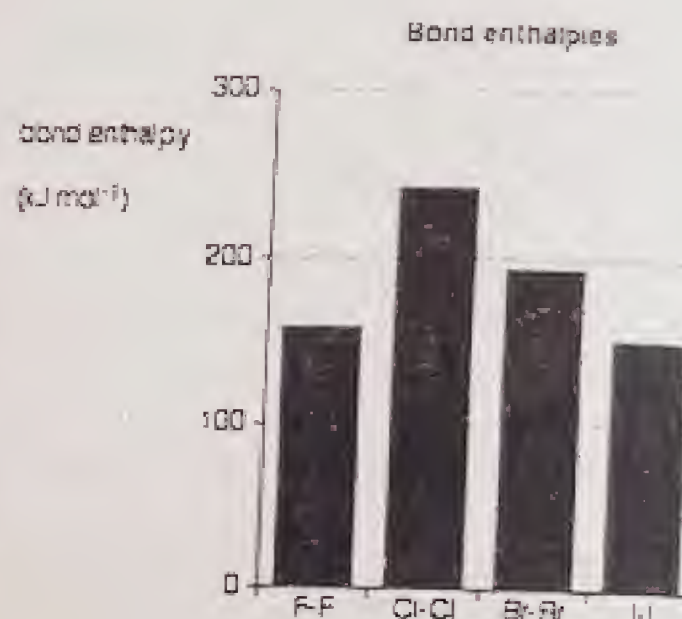
Gas not Liquid

### BOND ENTHALPY IN THE HALOGENS, $\text{X}_{2(g)}$

The bond enthalpies of the Cl-Cl, Br-Br and I-I bonds decreases down the group due to increase in atomic size except the F-F bond.

F-F bond has very low dissociation energy. It is due to following reasons

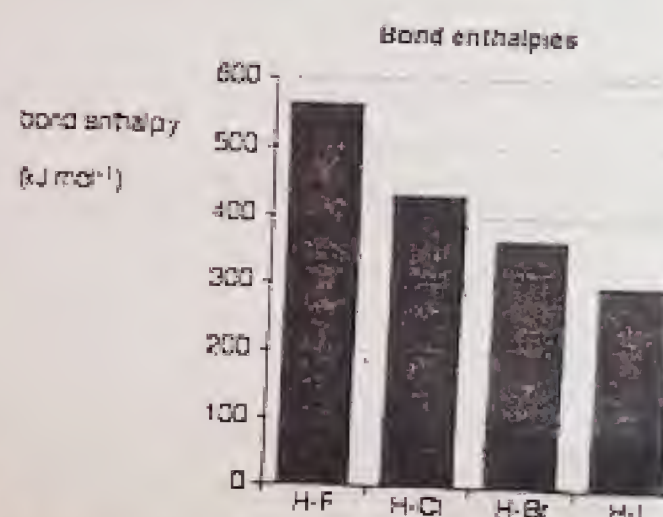
- It is due to very small F-F bond length than other X-X bond lengths. So, the F atoms in  $\text{F}_2$  molecule repel each other and thus the dissociation of  $\text{F}_2$  molecule into F atoms becomes easy.
- X-X bond in  $\text{Cl}_2$ ,  $\text{Br}_2$  and  $\text{I}_2$  molecules is stronger than F-F bond in  $\text{F}_2$  molecule. It is due to the possibility of the formation of multiple bonds in X-X bond with d-orbitals.



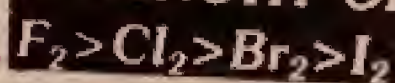
### BOND ENTHALPIES IN THE HYDROGEN HALIDES, $\text{HX}_{(g)}$

The bond enthalpies of HX decreases down the group

It is because, as the halogen atom gets bigger, the bonding pair gets more and more distant from the nucleus. The attraction is less, and the bond gets weaker. So the bond enthalpies of HX decreases down the group.



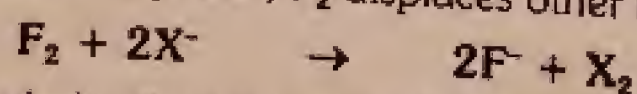
### STRENGTH OF HALOGENS AS OXIDIZING AGENTS:



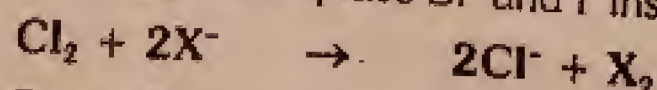
#### FACTS:

- A substance that has a tendency to accept one or more electrons is said to show oxidizing property.
- The halogens due to high electron affinity values have a great tendency to accept electron and hence act as strong oxidizing agent.
- The oxidizing property of a halogen molecule,  $\text{X}_2$  is represented by:
 
$$\text{X}_2 + \text{H}_2\text{O} \rightarrow \text{HX} + \text{HOX} \quad (\text{in this reaction, X takes electrons})$$
- During this reaction energy is released. This energy is made up from different energies like that of fusion, vaporisation etc.
- The values of energy decrease from  $\text{F}_2$  to  $\text{I}_2$ . Thus, the oxidizing power of halogens also decreases in the same direction. Thus, order of oxidizing power is
 
$$\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2 \quad (\text{weakest oxidizing agents}).$$

- Since  $\text{F}_2$  is the strongest oxidizing agent in the series, it will oxidize other halide ions to halogens in solution or when dry. i.e.,  $\text{F}_2$  displaces other halogens from their corresponding halides.



- Similarly  $\text{Cl}_2$  will displace  $\text{Br}^-$  and  $\text{I}^-$  ions from their solutions and  $\text{Br}_2$  will displace  $\text{I}^-$  ions from their solutions.





## THE ACIDITY OF THE HYDROGEN HALIDES

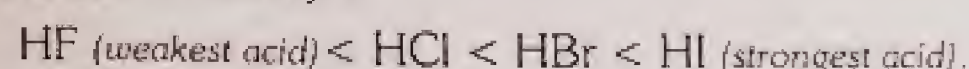
- All the halogen acids in the gaseous states are essentially covalent.

However, in the aqueous solution they ionise to give solvated proton ( $\text{H}_3\text{O}^+$ ) and hence acts as acids.



- HF ionises only slightly while HCl, HBr, and HI ionise completely. Hence HF is the weakest acid and strength of these acids increases from HF to HI.

The order of acidity is



- The weakest acidic nature of HF is due to the fact that the dissociation energy of H-F bond in HF molecule is the highest. Hence this molecule has least tendency to split up into  $\text{H}^+$  and  $\text{F}^-$  ions in aqueous solution.
- The above order of the acidic strength of HX acids can also be explained by relative order of the basicity of the conjugate bases of these acids. The order is  $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ . Since, a stronger conjugate base means a weaker acid, therefore the order of acidity of HX acids is  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ .
- The hydrides show no acidic character when perfectly dry.

## HALIDE IONS AS REDUCING AGENTS

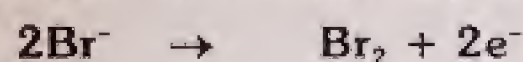
### TRENDS IN REDUCING STRENGTH ABILITY OF HALIDE IONS

(THE REDOX REACTIONS BETWEEN HALIDE IONS AND CONCENTRATED SULPHURIC ACID)

- Fluorides and Chlorides do not reduce concentrated sulphuric acid.

#### With bromide ions

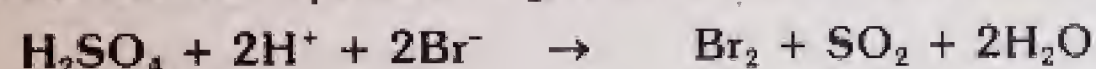
- ✓ The bromide ions are strong enough reducing agents to reduce the concentrated sulphuric acid.
- ✓ In the process the bromide ions are oxidized to bromine.



- ✓ The bromide ions reduce the sulphuric acid to sulphur dioxide gas.
- ✓ This is a decrease of oxidation state of the sulphur from +6 in the sulphuric acid to +4 in the sulphur dioxide.



- Combine these two half-equations to give the overall ionic equation for the reaction:



#### With iodide ions

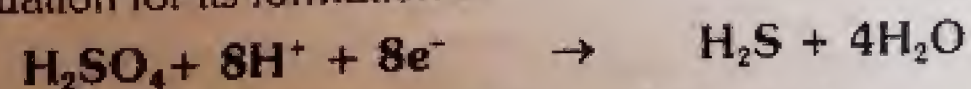
- ✓ Iodide ions are stronger reducing agents than bromide ions are.
- ✓ They are oxidized to iodine by the concentrated sulphuric acid.



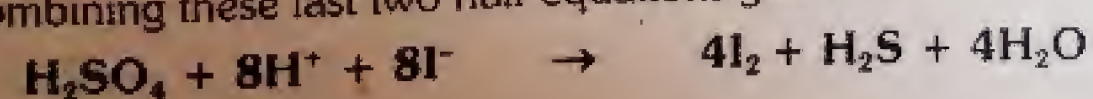
- The reduction of the sulphuric acid is more complicated than before. The iodide ions are powerful enough reducing agents to reduce it

- ✓ first to sulphur dioxide (sulphur oxidation state = +4)
- ✓ then to sulphur itself (oxidation state = 0)
- ✓ and all the way to hydrogen sulphide (sulphur oxidation state = -2).

- The most important of this mixture of reduction products is probably the hydrogen sulphide. The half-equation for its formation is:



- Combining these last two half-equations gives:





## SUMMARY

- Fluoride and chloride ions won't reduce concentrated sulphuric acid.
- Bromide ions reduce the sulphuric acid to sulphur dioxide. In the process, the bromide ions are oxidized to bromine.
- Iodide ions reduce the sulphuric acid to a mixture of products including hydrogen sulphide. The iodide ions are oxidized to iodine.
- Reducing ability of the halide ions increases as you go down the Group.

### Explanation

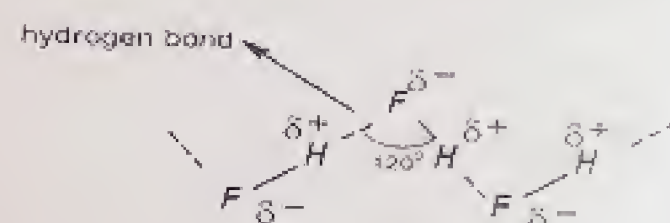
- When a halide ion acts as a reducing agent, it gives electrons to something else. That means that the halide ion itself has to lose electrons.
- The bigger the halide ion, the further the outer electrons are from the nucleus, and the more they are screened from it by inner electrons. It therefore gets easier for the halide ions to lose electrons as you go down the Group because there is less attraction between the outer electrons and the nucleus.

## QUICK QUIZ-11

### (1) Give reasons of the following

- **HI is stronger acid than HF.**

It can be explained on following bases



- In HF, molecules are Hydrogen-bonded in a zigzag manner. Thus, H-atom is entrapped between two F atoms as shown in the fig. So,  $H^+$  ion cannot be donated easily.
- The bond energy of H-F bond is considerably greater than H-I bond. Thus, HF cannot donate its  $H^+$  ions easily.
- The conjugate base of HF is  $F^-$  ion which is a stronger base than  $I^-$  ion. Thus its corresponding acid, HF, will be weaker than HI.

Hence, HI is a stronger acid than HF.

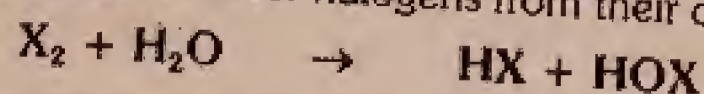
- **Although H-bonding in HF is stronger than that in  $H_2O$ ,  $H_2O$  has much higher b.pt.**  
It is because, HF can make one hydrogen bond per molecule while water can make two hydrogen bond per molecules. So, due to strong hydrogen bonding in water, it has higher boiling point than HF.
- **The acidic character of hydrides of VIIA elements increases on descending of the group.**
  - ✓ It is because down the group bond energy of H-X bond decreases, so the ease of donation of proton increases.
  - ✓ Moreover, the order of basicity of their conjugate bases is  $F^- > Cl^- > Br^- > I^-$ . Since, a stronger conjugate base means a weaker acid, therefore, the order of acidity of HX acids is  $HF < HCl < HBr < HI$ .  
Hence acidity increases down the group.

### (2) Illustrate the oxidizing properties of halogens by giving example of two typical reactions.

A substance that has a tendency to accept one or more electrons is said to show oxidizing property.

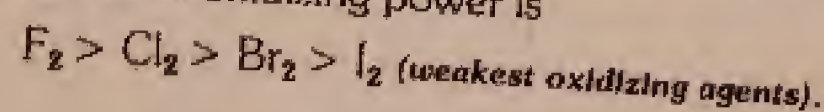
The halogens have high electron affinity values and also high hydration energy values of their ions. Thus, they have a great tendency to accept electron and hence act as strong oxidizing agent.

e.g.  $F_2$  displaces other halogens from their corresponding halides.



### (3) Arrange the halogens in the decreasing order of their oxidizing power.

The order of oxidizing power is





(4) Give reasons for the following:

(a) Chlorine is a stronger oxidizing agent than iodine.

It is due to two reasons

- The electron affinity of Cl is higher than that of iodine, so Cl will take up electron readily
- The hydration energy of  $\text{Cl}^-$  ion is higher than  $\text{I}^-$  ions due to smaller size. So, the  $\text{Cl}^-$  ion will form readily in solution. This is the main factor

It means, the chlorine will take up electrons readily to form  $\text{Cl}^-$  ions than iodine. Hence, chlorine is a stronger oxidizing agent than iodine.

(b) Halogens are the best oxidizing agents.

A substance that has a tendency to accept one or more electrons is said to show oxidizing property

The halogens have high electron affinity values and also high hydration energy values of their ions. Thus, they have a great tendency to accept electron to form anions and hence act as strong oxidizing agent

e.g.



(c) Fluorine is a better oxidizing than chlorine.

It is due to two reasons.

- The bond dissociation energy of fluorine is quite low, so it will dissociates rapidly to take up electron
- The main factor, however, is hydration energy. The  $\text{F}^-$  ions have high hydration energy due to small size, so it will form readily in solution. Thus fluorine will take up electrons readily to form  $\text{F}^-$  ions than chlorine. Hence, fluorine is a much stronger oxidizing agent than chlorine.

(d) Electronegativity of halogens decreases in the order  $\text{F} > \text{Cl} > \text{Br} > \text{I}$

It is due to increase in size of halogens down the group.

Due to increase in size, the distance of bonding pair increases from the nucleus of an atom. Hence, bonding pairs are less strongly attracted and so, the electronegativity decreases.

## SOCIETY, TECHNOLOGY AND SCIENCE

### Food and Beverage Canning

#### History

As early as 1940, can manufacturers began to explore adapting cans to package carbonated soft drinks. Two important points were investigated for their production.

(1) The can had to be strengthened to accommodate higher internal can pressures created by carbonation (especially during warm summer months). It means increasing the thickness of the metal used in the can ends. Otherwise, distortion of the end would strain the seal, creating potential leaks or making cans unstackable for storage and transit.

(2) Another concern for the new beverage can was its shelf life. Even small amounts of dissolved tin or iron from the can could impair the drinking quality of both beer and soft drinks.

Fortunately, beer, which is only mildly acidic, is relatively noncorrosive. In addition, beer ages naturally, so it has a limited shelf life of about three months in any package.

In contrast, the food acids, including carbonic, citric and phosphoric, in soft drinks present a risk for rapid corrosion of exposed tin and iron in the can.

The consequences of off-flavors, color changes and leakage through the metal needed to be addressed. At this point, the can was upgraded by improving the organic coatings used to line the inside, making cans heavier and more encasing.



## ELEMENTS/METALS - THEIR MINING AND EXTRACTION

Different elements/metals are not obtained such rather these are obtained after passing through different steps. These steps are:

- (1) Mining and enrichment
- (2) Reduction
- (3) Refining and Casting

In fact some special methods are used to obtain each metal from its ores and to develop it into useful articles. However, few steps are common in the metallurgy of every metal. These are follows.

### (1) MINING

#### (i) Crushing

- Obtaining ores by digging the rocks and hills is called mining.
- This work is done by engineers and laborers with the help of machines.
- But before this work it is confirmed by survey and analysis that obtaining metals from this is economic or not.

#### (ii) Grinding

- Breaking of rocks and larger stones into smaller size stones is called crushing.
- This is done by jaw crushers.

#### (iii) Hand Picking, Jugging and Shaking

- In Pakistan and other under developed countries where labour is cheap, metallic stones are picked and separated by hands.
- Heavy metals are separated from useless material i.e. gangue, by shaking with "chaage".
- In some countries this process is done by pressurized water.

#### (iv) Magnetic Separation

- The ground ore is passed over a magnetic belt which separates the magnetic metal from gangue.
- This process is used for metals which have magnetic properties like iron.

### (2) REDUCTION

- For the complete separation of a metal from gangue, ores are heated at high temperature.
- At its melting point, molten metal is separated from solid gangue.
- Different metals are mixed with different compounds according to the type of impurities present in the metal ore.
- Then they are passed through the process of reduction.
- The process of reduction is carried out in the blast furnace.

#### Blast Furnace

- It is lined inside with fire bricks.
- Its height and capacity are kept according to the requirement.
- Hot gases enter from lower side and ores are charged from the top of the furnace.
- Temperature is maintained at  $1500^{\circ}\text{C}$ - $3000^{\circ}\text{C}$ .
- This furnace is usually used for iron and copper metallurgy.

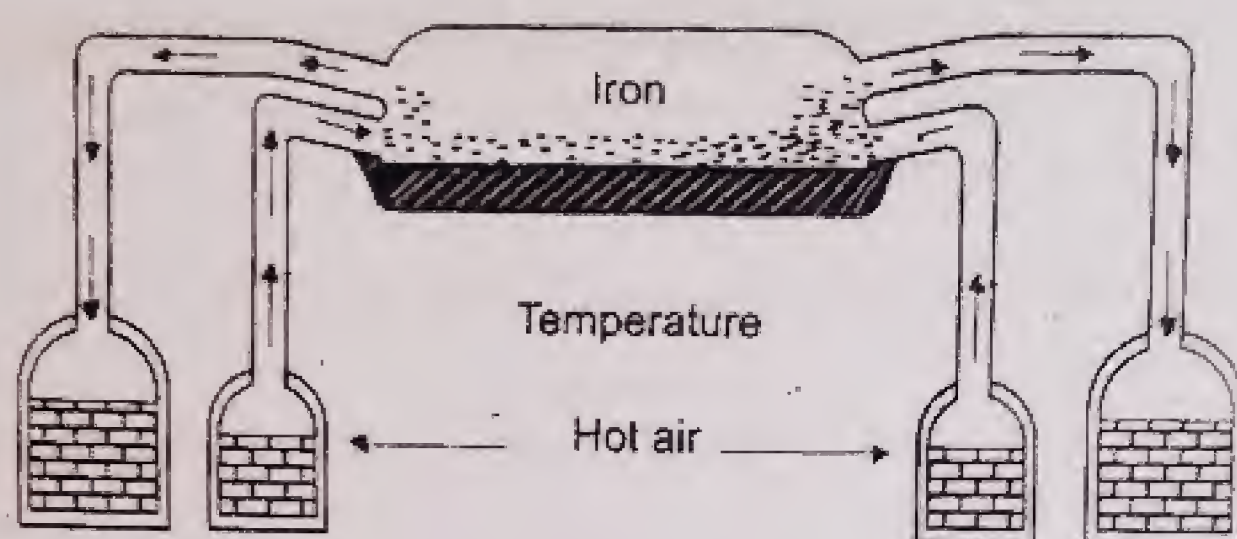


**REFINING OF METALS**

Metals extracted in the above process are further refined by the following process.

**Open-Hearth Process:**

- A fire furnace is used to remove the impurities of metal.
- It is lined inside with fire bricks and is just like a room.
- Burning gases are entered from one side and exhaust gases are removed from the opposite end. The process is operated from opposite ends after an interval. Metals melt in a shorter time by this two way heating.

**APPLICATIONS OF BLEACHING POWDER.**

- Bleaching powder is actually a mixture of calcium hypochlorite ( $\text{Ca}(\text{OCl})_2$ ) and the basic chloride  $\text{CaCl}_2 \cdot \text{H}_2\text{O}$  with some slaked lime,  $\text{Ca}(\text{OH})_2$ .
- Bleaching powders take time to dissolve in water and longer to work. But, it has a longer shelf life in comparison to liquid bleaches and can be used on items like upholstery, carpet and some delicate fabrics.
- However, bleaching powder should never be combined with ammonia or used on colored fabrics as it will cause fading.
- Bleaching powder is used for bleaching cotton and linen. It is also used in bathroom cleaners, household disinfectant sprays, moss and algae removers, and weedkillers.
- Bleaching powder is highly effective for cleaning inside the home and outdoors.
  - ✓ It can be used for removing mildew from fabric, cleaning countertops and for removing mold from grout between tiles, bathmats and shower curtains.
  - ✓ Outside, the agent can be used on plastic furniture, unpainted cement, paving and painted surfaces to eliminate mildew and other stubborn stains.
- Bleaching powder can be used to safely disinfect.
  - ✓ It can sterilize many things around the home including secondhand goods, trash cans, pet accessories and baby toys and furniture.
  - ✓ Bleaching powder is a highly effective means of returning the luster to white porcelain and glassware. Glassware can regain its sparkle by adding a small amount of powdered bleach to dishwater when washing glasses.
- Gardening
  - ✓ To kill any annoying weeds growing from cracks and crevices in the garden a strong mixture of bleaching powder and water is applied.
  - ✓ Moss and algae on garden walkways can be easily eliminated by scrubbing with bleaching powder diluted in water.
  - ✓ Powdered bleach is also useful for sanitizing garden tools to avoid diseases spreading between plants.
  - ✓ Adding powdered bleach to the water of cut flowers will help to preserve their freshness by preventing the growth of bacteria in the vase.



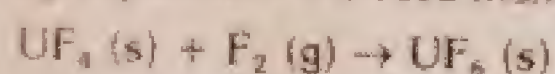
- Bleaching powder is used for the disinfection of drinking water or swimming pool water. It is used as a sanitizer in outdoor swimming pools in combination with a cyanuric acid stabilizer, which reduces the loss of chlorine due to ultraviolet radiation.
- The calcium content hardens the water and tends to clog up some filters; hence, some products containing calcium hypochlorite also contain anti-scaling agents.
- In addition, bleaching powder may be used to manufacture chloroform.
- Bleaching powder is used also in sugar industry for bleaching sugar cane juice before its crystallization.

## COMMERCIAL USES OF HALOGENS

- Chlorine is used as a cheap industrial oxidant in the manufacture of bromine.
- Iodine is dissolved in alcohol, commonly known as tincture of iodine. It is used as a mild antiseptic for cuts and scratches. Iodine is also mixed with the detergents used in cleaning dairy equipment.

- Small quantities of fluorine are used in rocket propulsion.

Much larger quantities are used to make uranium (VI) fluoride for the separation of  $^{238}\text{U}$  and  $^{235}\text{U}$ :



- Fluorine is also used to make a wide range of fluorocarbon compounds for use as refrigerants, aerosol propellants, anaesthetics and fire-extinguisher fluid.

One of the most important fluorocarbons is poly (tetrafluoroethene), PTFE, frequently sold under the trade name Fluon or Teflon.

## IODINE DEFICIENCY AND GOITER

### Iodine Deficiency

- Iodine is an element that is needed for the production of thyroid hormone. The human body cannot synthesize iodine, so it is an essential element.
- The deficiency of iodine leads to enlargement of thyroid a condition called goiter.
- Hypothyroidism and mental retardation in children and infants is observed if their mothers suffered from iodine deficiency during pregnancy.
- Before 1920, iodine deficiency was common in Appalachian, north-western US regions, and in most of Canada. Approximately, 40% of the world's population remains at the risk of iodine deficiency.

### Goiter:

- The term goiter refers to the abnormal enlargement of thyroid gland due to deficiency of iodine in diet.
- It results in swelling in neck.
- It is important to know that the presence of goiter does not necessarily mean that the thyroid gland is malfunctioning (hypothyroidism). A goiter can also occur in a gland that is producing too much thyroid hormone (hyperthyroidism) or even the correct amount of hormone (euthyroidism).
- A goiter indicates there is a condition present which is causing the thyroid to grow abnormally.

## FLUORIDE DEFICIENCY AND TOXICITY

### FLUORIDE TOXICITY

- Fluoride toxicity or fluoride poisoning is a condition in which more fluoride is taken than the amount required for normal growth, development and metabolism.
- Fluoride toxicity is characterised by a variety of signs and symptoms.



- Poisoning most commonly occurs following ingestion of conspicuous amount of fluoride entraining products
- Symptoms or set usually occurs within minutes of exposure
- Fluoride is found in many common household products e.g. tooth paste, dietary supplement, insecticides, rodenticides etc.
- Fluoride toxicity results
  - (i) Arthritis
  - (ii) Stiff painful joints with or without swelling
  - (iii) Asthma, especially after showering
  - (iv) Painful bony lumps where tendons and ligaments attach to bones

#### FLUORIDE DEFICIENCY

- Fluoride deficiency results when the amount of its up take is less than required.
- Fluoride deficiency results in
  - (i) Brittle bones or demineralization of bones
  - (ii) Cavities
  - (iii) Weakened tooth enamel
  - (iv) Fluoride deficiency can lead to a higher likelihood of developing bone fractures and possibly even osteoporosis.

Halogens and their compounds are used or bleaching, refrigeration and as aerosols, etc.

### QUICK QUIZ-12

#### (1) How different metals are extracted

Different metals are extracted after passing through different steps. These steps are

- (i) Mining and enrichment
- (ii) Reduction
- (iii) Refining and Casting

#### (2) What problems are caused by fluorine deficiency

Fluorine deficiency results in

- (i) Brittle bones or demineralization of bones
- (ii) Cavities
- (iii) Weakened tooth enamel
- (iv) Fluorine deficiency can lead to a higher likelihood of developing bone fractures and possibly even osteoporosis

#### (3) What is goiter?

The term goiter refers to the abnormal enlargement of thyroid gland due to deficiency of iodine in diet. It results in swelling in neck. A goiter indicates there is a condition present which is causing the thyroid to grow abnormally.

It is important to know that the presence of goiter does not necessarily mean that the thyroid gland is malfunctioning (hypothyroidism). A goiter can also occur in a gland that is producing too much thyroid hormone (hyperthyroidism) or even the correct amount of hormone (euthyroidism).

#### (4) How fluoride is useful for uranium separation

Large quantities of fluorine are used to make uranium (VI) fluoride for the separation of  $^{235}\text{U}$  and  $^{238}\text{U}$ .





## KEY POINTS

- Alkali metals have only one electron in s-orbital of their valence shell. They lose one electron of the valence shell forming monovalent positive ions.
- Alkaline earth metals have two electrons in s-orbital of their valence shell.
- They lose two electrons forming divalent positive ions  $M^{2+}$ .
- Lithium behaves different from the other alkali metals.
- Beryllium is the only member of group 2 which reacts with alkalies to give hydrogen. The other members do not react with alkalies.
- Nitrates of lithium, magnesium and barium on heating give oxygen, nitrogen peroxide and the corresponding metallic oxides.
- The pair of outermost electrons that does not readily take part in chemical combination is termed as inert pair.
- The electronic configuration of group 4 elements show that they have four electron in their valence shells, two electron of which are in s-orbital and the remaining two are in p-orbitals.
- The halogens are very reactive. Intermolecular forces in halogens increase down the group, fluorine is a gas but iodine is solid.
- They form ionic compounds with s-block metals, covalent compound with p-block elements and complex ions with d-block metals. Fluorides are usually ionic.
- They show oxidation states -1, +1, +3, +5, +7 but fluorine shows the oxidation state of -1 only.
- Oxidizing power of halogens decreases down the group in the following order:  $F_2 > Cl_2 > Br_2 > I_2$
- Reducing power of halide ions decrease from  $I^-$  to  $Br^-$ . Chloride and fluoride ions are not reductants.



# EXERCISE

Q1: Select the right answer from the choices given with each question.

- (i) Oxides and hydroxides of Group I elements are:  
(a) Acidic (b) Alkaline (c) Neutral (d) Amphoteric
- (ii) The flame colour of sodium metal or its compounds is  
(a) bright crimson (b) violet (c) golden yellow (d) bright blue
- (iii) When sodium burn in air, it forms sodium:  
(a) Monoxide (b) Peroxide (c) Oxide (d) Superoxide
- (iv) The carbonates of alkali metals are not affected by heat except:  
(a)  $\text{Li}_2\text{CO}_3$  (b)  $\text{Na}_2\text{CO}_3$  (c)  $\text{K}_2\text{CO}_3$  (d)  $\text{Rb}_2\text{CO}_3$
- (v) Green is characteristic flame color of  
(a) calcium (b) barium (c) strontium (d) sodium
- (vi) All the carbonates, sulphates and phosphates of alkaline earth metals are ..... In water.  
(a) sparingly soluble (b) soluble (c) insoluble (d) less soluble
- (vii) The first ionization energy is higher for the  
(a) Alkaline earth metals (b) alkali metals (c) halogens (d) noble gases
- (viii) Which one of the element has the maximum electron affinity?  
(a) F (b) Cl (c) Br (d) I
- (ix) Which pair has both members from same period of periodic table?  
(a) Na-Ca (b) Na-Cl (c) Ca-Cl (d) Cl-Br
- (x) Melting points and boiling points of alkali metals  
(a) decreases from top to bottom (b) increase from top to bottom  
(c) first increases then decreases (d) remains unchanged
- (xi) Which one of the following oxides is Amphoteric in nature  
(a) Rubidium oxide (b) Barium oxide (c) Antimony oxide (d) Sulphur oxide
- (xii) Oxidizing power of halogen depends upon  
(a) energy of dissociation (b) electron affinity (c) heat of vaporization (d) all of above
- (xiii) Which of following oxide is Amphoteric in nature?  
(a) MgO (b) BeO (c)  $\text{CO}_2$  (d)  $\text{SnO}_2$
- (xiv) Select the correct increasing order of atomic radius?  
(a)  $\text{Ne} > \text{O} > \text{S} > \text{Al}$  (b)  $\text{Ne} < \text{O} > \text{S} > \text{Al}$  (c)  $\text{Ne} < \text{O} < \text{S} < \text{Al}$  (d)  $\text{Ne} > \text{O} < \text{S} > \text{Al}$
- (xv) Due to inert pair effect ..... Oxidation state is more stable than ..... For Sn and P(b)  
(a) 2+, 4+ (b) 1+, 4+ (c) 4+, 2+ (d) 2+, 3+
- (xvi) Highest electron affinity is shown by?  
(a)  $\text{F}_2$  (b)  $\text{I}_2$  (c)  $\text{Br}_2$  (d)  $\text{Cl}_2$
- (xvii) Which is the strongest reducing agent?  
(a) HF (b) HCl (c) HI (d) HBr
- (xviii) Substance boiling at higher temperature among following is?  
(a) HI (b) HF (c) HCl (d) HBr
- (xix) Group VII-A elements are generally called:  
(a) Halogens (b) Noble gases (c) Inert gases (d) Metalloids
- (xx) The radioactive element in halogen group is:  
(a) Radon (b) Radium (c) Astatine (d) Bromine

## ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (b) Alkaline Group I elements are highly electropositive metals. So, they form alkaline oxides and hydroxide. e.g. $\text{Na}_2\text{O}$ and $\text{NaOH}$ .	(ii) Ans: (c) golden yellow Sodium salts give golden yellow colour to flame
(iii) Ans: (b) Peroxide Sodium form sodium peroxide: i.e., $\text{Na} + \text{O}_2 \rightarrow \text{Na}_2\text{O}_2$	(iv) Ans: (a) $\text{Li}_2\text{CO}_3$ $\text{Li}_2\text{CO}_3$ decomposes on heating $\text{Li}_2\text{CO}_3 \rightarrow \text{Li}_2\text{O} + \text{CO}_2$



<b>(v) Ans: (b) barium</b> Barium salts give apple green colour to flame.	<b>(vi) Ans: (d) less soluble</b> The carbonates, sulphates and phosphates of s-block metals are less soluble in water than those of p-block metals. However, the solubility of these decreases down the group.
<b>(vii) Ans: (d) noble gases</b> Noble gases being completely inert, therefore, it is very difficult to remove their electrons. So, they have highest first ionization energies. Moreover, in any period they have highest nuclear charge as well.	<b>(viii) Ans: (b) Cl</b> The electron affinity values decreases down the group. However, the electron affinity of F is less than Cl due to small size. Hence, among halogens, Cl has the highest value of electron affinity.
<b>(ix) Ans: (b) Na-Cl</b> Both Na and Cl are present in Period 3.	<b>(x) Ans: (a) decreases from top to bottom</b> It is due to increase in size down the group.
<b>(xi) Ans: (c) Antimony oxide</b> Antimony is known to show amphoteric as well as acidic and basic behaviour.	<b>(xii) Ans: (d) all of above</b> No trend is observed in the oxidizing power of halogens.
<b>(xiii) Ans: (b) BeO</b> BeO is amphoteric in nature, since it can react with both acids and bases to form salts.	<b>(xiv) Ans: (c) Ne &lt; O &lt; S &lt; Al</b> Ne and Cl are present in Period 3. Since, atomic size increases from left to right, so Ne is smaller than Cl. Similarly, size of S is smaller than Al. However, S and Al are present in Period 3, so they are larger in size than Ne and Cl.
<b>(xv) Ans: (a) 2+, 4+</b> The general configuration of f <sub>7</sub> and f <sub>9</sub> is $ns^2 (n-1)f^7$ . So, only $ns^2$ electrons are removed and $(n-1)f^7$ electrons remain intact. Hence, 2+ oxidation state is more stable than 4+ due to half-filled effect.	<b>(xvi) Ans: (d) Cl<sub>2</sub></b> Chlorine is more reactive than bromine and iodine.
<b>(xvii) Ans: (c) HI</b> It is because, HI has least bond energy among all HX. So, it gives hydrogen readily to reduce substances.	<b>(xviii) Ans: (b) HF</b> HF has highest boiling point due to strong hydrogen bonding.
<b>(xix) Ans: (a) Halogens</b> These form salts on reacting with metals, so they are called halogens. (Halo = salt, Gen = former).	<b>(xx) Ans: (c) Astatine</b> Astatine has unstable nucleus, so it emits radiations due to breakdown of nucleus and shows radioactivity.

**Q2: Give brief answers for the following questions.**

- ✓ (i) Although Na and P are present in the same period yet their oxides are different in nature.  $\text{Na}_2\text{O}$  is basic while  $\text{P}_2\text{O}_5$  is acidic why?  
Metal forms basic oxides while non-metal form acidic oxides. Since sodium is a metal, it will form basic oxide, i.e.  $\text{Na}_2\text{O}$ . When this oxide is dissolved in water, it forms  $\text{NaOH}$ , that is a base and solution becomes basic.



Phosphorus is a non-metal so it will form acidic oxide i.e.  $\text{P}_2\text{O}_5$ . When this oxide is dissolved in water, it produces  $\text{H}_3\text{PO}_4$ , which is an acid, and solution becomes acidic due to formation of  $\text{H}_3\text{PO}_4$ .



- ✓ (ii) How acidic basic and amphoteric behaviour of oxides is explained?

An amphoteric oxide shows both acidic and basic properties. e.g.  $\text{BeO}$

It reacts with acids to form salts



It also reacts with bases to form salts





(vi) **Why the elements of group 1 are called alkali metals?**

The word 'alkali' is an Arabic word means 'ashes'. This word was used by Arabs because they found that ashes of plant mainly consist of Na and K. So, they called these metals as alkali metals. The alkali metals include Li, Na, K, Rb, Cs and Fr. They produce strong alkaline solution with water.

(vii) **Why all group 1 metals have low ionization energies?**

In any period, Group 1 metals have larger size and least electronegativity. So, it is easy to remove their outermost electron. Hence, they have very low ionization energies. That is why they readily form positive ions. e.g.  $\text{Na}^+$ ,  $\text{K}^+$  etc.

(viii) **Why do the group 1 metals show strong electropositive character?**

Electropositivity is the ability to give electrons. Since, in any period, Group 1 metals have larger size and least electronegativity. So, it is easy to remove their outermost electron. Hence, they have very low ionization energies and show electropositive character. In Group 1 metals, the electropositivity increases down the group.

(ix) **Why do group 1 metals show strong reducing properties?**

In any period, Group 1 metals have larger size and least electronegativity. Thus, alkali metals can easily lose electrons i.e. they are easily oxidized. Thus they can reduce substances and act as excellent reducing agents.

(x) **Why different colours are imparted by the atoms of the group 1 metals to the flame?**

In alkali metal atoms the outer  $ns^1$  electron is loosely held with the nucleus. So, it can be easily excited to the higher energy levels by absorbing a small amount of heat energy. When this excited electron comes back to its original position, it gives out absorbed energy in the form of light in visible region of the electromagnetic radiations. Different amount of energy is absorbed in different atoms for excitation of electron. Thus, different colours are imparted by the atoms to the flame.

(xi) **Why the elements of group 2 are called alkaline earth metals?**

The alkaline earth metals are given this name because they form 'alkalies' in water and are widely distributed in 'earth' crust. These include Be, Mg, Ca, Sr, Ba & Ra.

(xii) **Why do the group 2 earth metals have high melting and boiling points than alkali metals?**

The melting and boiling points of Group 2 elements are higher than Group 1 elements. It is because Group 2 elements have two valence electrons. So, they form greater number of bonds than Group 1 elements.

(xiii) **How do group 1 metals resemble with group 2 metals.**

1. Both alkali and alkaline earth metals are s-block elements. Both have their outermost electron in s-orbital.
2. Elements of both groups are highly electropositive.
3. Elements of both groups do not occur free in nature.
4. Hydroxides of both alkali and alkaline earth metals are strongly basic.
5. On heating in Bunsen flame, elements of both groups impart characteristic colour to flame.

(xiv) **How do group 1 metals differ from group 2 metals?**

- |   |  |
|---|--|
| 1. They have one electron in their outermost s-orbital.               | 1. They have two electrons in their outermost s-orbital. |
| 2. They have low melting points than alkaline earth metals.           | 2. They have relatively high melting points              |
| 3. They have relatively larger atomic size.                           | 3. They have relatively smaller atomic size              |
| 4. The alkali metals are relatively softer than alkaline earth metals | 4. They are relatively harder.                           |
| 5. They have relatively low values of ionization                      | 5. They have relatively high values of ionization        |



energies.	energies
6. Their oxides and hydroxides are more ionic in nature.	6. Their oxides and hydroxides are less ionic in nature.
7. They decompose water vigorously at room temperature. $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2$	7. They decompose water less vigorously. $\text{Mg} + \text{H}_2\text{O} \rightarrow \text{MgO} + \text{H}_2$
8. Their carbonates, sulphates and phosphates are soluble in $\text{H}_2\text{O}$ except Li	8. Their carbonates, sulphates and phosphates are mostly insoluble in $\text{H}_2\text{O}$
9. They are highly electropositive	9. They are relatively less electropositive
10. Their hydroxides are strongly basic	10. Their hydroxides are relatively less basic.
11. On heating, their nitrates give nitrites and oxygen except Li. $2\text{NaNO}_3 \rightarrow 2\text{NaNO}_2 + \text{O}_2$	11. On heating, their nitrates give oxides, nitrogen peroxide and oxygen $2\text{Ca}(\text{NO}_3)_2 \rightarrow 2\text{CaO} + 4\text{NO}_2 + \text{O}_2$

**(xii) Discuss the metallic and non-metallic character of group 4 elements.**

The metallic character increases down the group in Group 4 elements.

- Carbon, Silicon and Germanium has covalent structures.
- "Grey tin" or "alpha-tin" also shows covalent bonding.
- The "white tin" or "beta-tin" is metallic. In this form atoms are held together by metallic bonds in a close-packed arrangement. In close-packing, each atom is surrounded by twelve (12) near-neighbours.
- Lead also shows metallic bonding.

Thus, a clear trend is found down the group from the typical covalency in non-metals to the metallic bonding in metals.

**(xiii) Discuss the general group trends of group 7 elements.**

- Atomic radius, melting points and boiling points increases down the group due to increase number of shells, greater shielding effect and less nuclear charge.
- Electronegativity, electron affinity values decreases down the group due to increase in atomic size.
- The bond enthalpies of the Cl-Cl, Br-Br and I-I bonds decreases down the group due to increase in atomic size except the F-F bond.
- The oxidizing power decreases down the group.

**(xiv) Why the term halogen is used for group 7 elements?**

These form salts on reacting with metals, so they are called halogens. (Halo = salt, Gen = former).

e.g.  $2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl}$

Other examples: KBr, NaF, LiCl, RbCl etc.

**(xv) Why does fluorine differ from other members of its group?**

Fluorine differs from its family members due to

- Small size of F atom and  $\text{F}^-$  ion
- High first ionization energy and electronegativity
- Low dissociation energy of  $\text{F}_2$  molecule as compared to  $\text{Cl}_2$  and  $\text{Br}_2$
- Valence shell restriction to an octet.

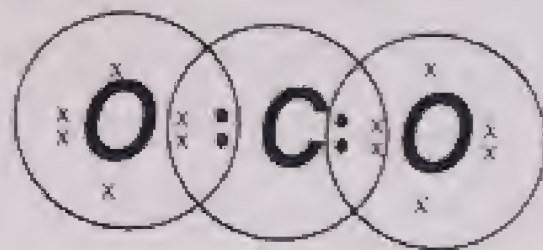
**Differences**

- F has very small size. Thus it can form effective overlap with other elements except N, O and itself. Thus it can form shorter and stronger bonds
- Ionic fluorides have very high lattice energies than other halides, thus these are stable. It is due to this reason that fluorides of Ca, Mg, Ba and Sr are insoluble in water
- $\text{F}_2$  molecule has very low dissociation energy. Thus it is very reactive, other halogens react very slowly under similar conditions.
- Since valence shell of F is restricted to an octet. Therefore, many of its compounds show inertness e.g.  $\text{CF}_4$ ,  $\text{SF}_6$  etc.
- Due to restriction to an octet, F shows only -1 oxidation state, while other halogens show variable oxidation states.
- Only F reacts with noble gases directly like Xe and Rn to give fluorides.



(xvi) What is the structure of  $\text{CO}_2$  and  $\text{SiO}_2$  and why they differ?

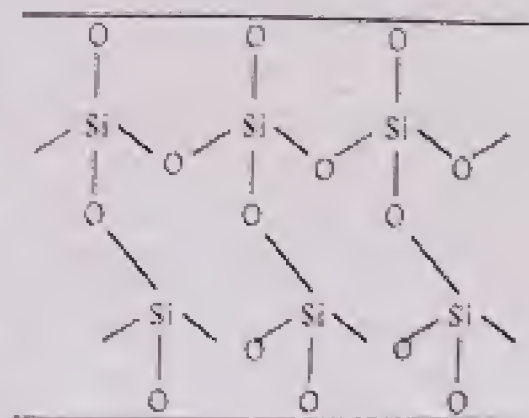
- The  $\text{CO}_2$  exist in molecular form with weak intermolecular forces. Its dipole moment is zero, therefore it is a linear molecule. Due to weak forces it exists as gas at room temperature.



- The  $\text{SiO}_2$  is a macromolecular compound. In this silicon and oxygen atoms are linked together covalently in continuous chains. Thus, silicon dioxide is a non-volatile and hard solid unlike carbon dioxide.

The difference in structure of  $\text{SiO}_2$  and  $\text{CO}_2$  is due to the following two reasons

- Silicon atoms are much larger in size than carbon atoms and thus tend to be surrounded by more oxygen atoms.
- Silicon forms only single bond with oxygen atoms while carbon forms double bonds.



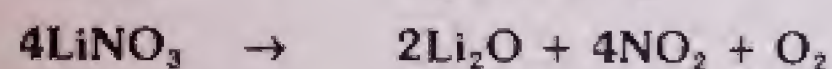
(xvii)  $\text{CO}_2$  is a gas while  $\text{SiO}_2$  is a solid although C and Si belong to the same group?

The  $\text{CO}_2$  exist in molecular form with weak intermolecular forces. Its dipole moment is zero, therefore it is a linear molecule. Due to weak forces it exists as gas at room temperature.

The  $\text{SiO}_2$  is a macromolecular compound. In this silicon and oxygen atoms are linked together covalently in continuous chains. Thus, silicon dioxide is a non-volatile and hard solid.

(xviii) Explain why nitrates and carbonates of Li are not stable?

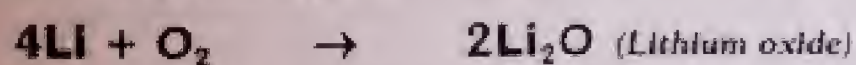
The nitrates and carbonates of Li are decomposed on heating.



Li has small size. So, the gain in electrostatic attraction while converting to oxide is considerable. In case of large cation like  $\text{K}^+$ , the gain in electrostatic attraction is relatively much less and the decomposition is difficult.

(xix) Differentiate the behaviour of Li and Na with atmospheric oxygen.

Lithium burns in atmospheric oxygen to form the normal oxide,  $\text{Li}_2\text{O}$



Sodium burns in atmospheric oxygen to form the peroxide.



(xx) Alkali metal carbonates are more soluble than alkaline earth metal carbonates. Why?

The alkali metal cations have relatively larger ionic size than alkaline earth metal cations. Moreover, they have  $\text{M}^+$  ions. Therefore, in carbonates, they have loose packing of ions weak forces. So their lattice energies are very low. Hence, they dissociate in water easily.

That is why alkali metal carbonates are more soluble than alkaline earth metal carbonates.

(xxi) Explain why stability solubility of alkaline earth metal carbonates decrease down the group?

In alkaline earth metals, the ionic size increases down the group. Moreover, carbonate anion is itself a bulky (large) anion. Generally, larger the size of ion, lesser is the hydration and solubility. So, due to difficulty in hydration of ions, the solubility of alkaline earth metal carbonates decreases down the group.



(xxii) Oxidizing power of  $F_2$  is greater than  $I_2$ . Why?

It is due to three reasons.

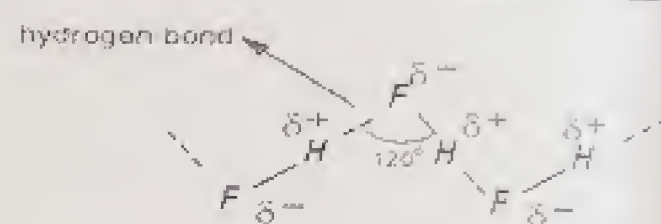
- The bond dissociation energy of fluorine is quite low, so it will dissociates rapidly to take up electron
- The electron affinity of F is greater than I, so it will take up electron more readily.
- The  $F^-$  ion has high hydration energy due to small size, so it will form readily in solution. Actually, this is the main factor

It means that fluorine will take up electrons readily to form  $F^-$  ions than iodine. Hence, fluorine is a much stronger oxidizing agent than iodine.

(xxiii) HF is weak acid than HI. Why?

In HF, molecules are Hydrogen-bonded in a zigzag manner. Thus, H-atom is entrapped between two F atoms as shown in the fig.

Moreover, the bond energy of H-F bond is considerably greater than H-I bond. Thus, HF cannot donate its  $H^+$  ions easily, hence it is a weaker acid.

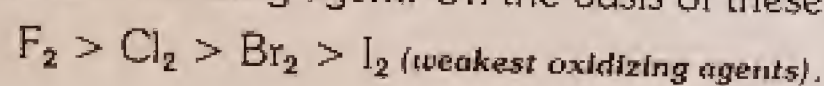


(xxiv) On what factors does the oxidizing power of halogens depend?

Following factors affect oxidizing power

- (a) Energy of dissociation      (b) Electron affinities of atoms      (c) Hydration energy of ions

If a halogen has low energy of dissociation, high electron affinity and high hydration energy of its ions, then it will be a better oxidizing agent. On the basis of these factors, the order of oxidizing power is



**Q3: Give detailed answers for the following questions**

(i) (a) The pattern of first ionization energy and melting and boiling point is not smooth. Justify it.

Ionization Energies:

In a group in periodic table, the irregularity is due to the filling of the d-orbitals and f-orbitals in lower members of the group. Since d and f-orbitals have poor shielding effect, so they cannot shield the valence electron effectively. Hence, the pattern becomes irregular.

Melting and Boiling points:

Melting and boiling points largely depends upon the structure of elements.

e.g. Group 1 and 2 elements exist as metallic crystals. Thus, the melting points and boiling points of group 1 and 2 elements decrease from top to bottom due to increase in size. It is because larger size atoms have weaker forces than smaller size atoms.

However, non-metals of groups 7 exists as molecular substances. So, melting points and boiling points increase from top to bottom. It is because, molecular size increases down the group. Larger molecules have greater polarizability, therefore, these have stronger intermolecular forces. Thus melting points and boiling points increases down the group. Thus pattern of melting and boiling points is not smooth.

(b) Why atomic radius increases in group and decreases along the period.

- The number of shells in all the elements of a given periods remains the same.
- The value of effective nuclear charge, increases from left to right due to increase in number of protons.
- The increased effective nuclear charge pulls the electron cloud of the atom nearer to the nucleus and thus the size of the atoms and ions goes on decreasing from left to right.

The atomic radius increases down the group from lithium to caesium. It is because, down the group number of shells increases. So, the atomic volume increases. Hence, atomic and ionic radii (of  $M^+$  ions) increases from lithium to caesium.



(c) Describe the trends in reaction of period 3 elements with water.  
See Page 7

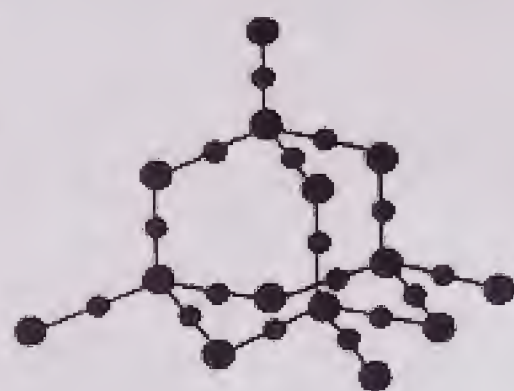
(d) The melting and boiling points of the elements increase from left to right up to the middle in period 3 elements and decrease onward. Why?  
See Page 6

(iii) Discuss the metallic oxides and silicon dioxide under the following headings:

(a) Structures

Metallic oxides: Sodium, magnesium and aluminium oxides structure/diagram is same as sodium chloride.

Silicon dioxide: Crystalline silicon has the same structure as diamond. In this structure atoms of both silicon and oxygen are present. In  $\text{SiO}_2$ , each silicon atom is bridged to its neighbouring silicon by an oxygen atom.



(b) Melting and Boiling points

Metallic oxides and silicon dioxide have giant structures. Thus they have high melting and boiling points. It is because a lot of energy is needed to break the strong bonds (ionic or covalent) operating in three dimensions.

(c) Electrical conductivity.

Metallic oxides: Metallic oxides are ionic in nature. They cannot conduct electricity in solid state because there are no free ions or electrons in solid state.

However, the ionic oxides can conduct electricity in molten state. It is because free ions are present in molten state. These ions show movement towards the electrodes where they discharge themselves.

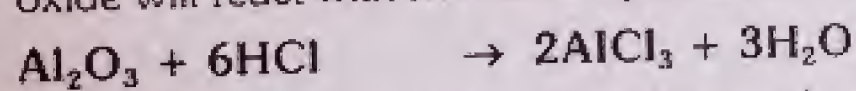
Silicon dioxide: In  $\text{SiO}_2$ , all four electrons of Si are used in forming covalent bonds. Hence, there are no free ions or electrons in  $\text{SiO}_2$  so it will not conduct electricity.

(iii) Discuss acid-base behaviour of

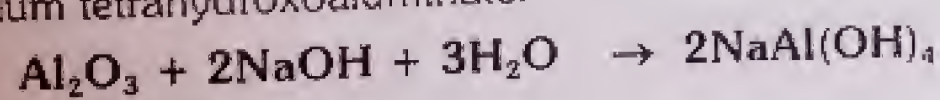
(i) Aluminium oxide

It is an amphoteric oxide. It gives reactions as both a base and an acid.

Aluminium oxide will react with hot dilute hydrochloric acid to give aluminium chloride solution.

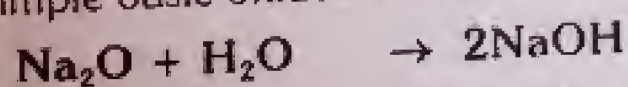


With hot, concentrated sodium hydroxide solution, aluminium oxide reacts to give a colourless solution of sodium tetrahydroxoaluminate.

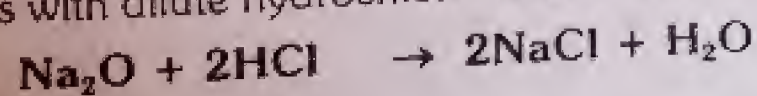


(ii) Sodium oxide

It is a simple basic oxides. It reacts with water to give the sodium hydroxide.



It reacts with dilute hydrochloric acid to give colourless sodium chloride solution and water.



(iv) (a) Why are different types of oxides formed as you go down the group?

(b) How Beryllium differs from other members of its group?

(c) Why is Beryllium chloride covalent and not ionic?

Beryllium is more electronegative and less electropositive than its family members. So, it does not lose its electron readily. Hence, it will not form ionic bond with chlorine. Instead, it will share its electrons with chlorine to form Beryllium chloride which will be covalent in nature.



(v) (a) Why do some metals form peroxides on heating in oxygen?

The peroxide ion has a weak covalent bond between two oxygen atoms. Small size metal ions have high charge density. So, when they come closer to peroxide ion, they polarize it so much that peroxide ion is broken. e.g.  $\text{Li}^+$ ,  $\text{Be}^{+2}$ ,  $\text{Mg}^{+2}$  have high charge density due to smaller size so they cannot form peroxides. The metals which have larger atomic size have low charge density, so they can form peroxides. e.g.  $\text{Na}^+$ ,  $\text{Ba}^{+2}$

(b) Why do group 2 elements form nitrides on heating in air?

To form a group 2 metal nitride, energy is given for two purposes, i.e. (i) to form  $\text{M}^{+2}$  ion and (ii) to break and convert nitrogen molecule into nitride ion ( $\text{N}^{3-}$ ). Since,  $\text{M}^{+2}$  ions are small size so they have high charge density and hence develop strong attractions for  $\text{N}^{3-}$  ion. Therefore a lot of energy is released as lattice energy. As a result, the energy given to form ions is compensated by the release of energy during lattice formation. Hence, the reaction becomes energetically favourable. Therefore, group 2 elements form nitrides. Similarly Li also form nitride.

(c) Discuss the trend in solubility of hydroxide of group 2 elements.

The solubility of Group 2 hydroxides increases down the group as shown by the solubility products.

$$\text{Be}(\text{OH})_2 = 1.6 \times 10^{-26}$$

$$\text{Mg}(\text{OH})_2 = 8.9 \times 10^{-12}$$

$$\text{Ca}(\text{OH})_2 = 1.3 \times 10^{-4}$$

$$\text{Sr}(\text{OH})_2 = 3.2 \times 10^{-4}$$

$$\text{Ba}(\text{OH})_2 = 5.4 \times 10^{-2}$$

- Thus,  $\text{Be}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$  are almost insoluble in  $\text{H}_2\text{O}$ .
- The hydroxides of other metals are slightly soluble.

It is because, lattice energy decreases down the group due to increase in size.

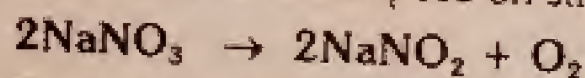
(vi) Discuss the trends in thermal stability of the carbonates and nitrates.

Group 1 compounds are more stable to heat than the corresponding compounds in Group 2.

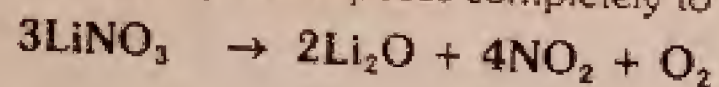
The lithium compounds behave similarly to Group 2 compounds.

The rest of Group 1 behave similarly but in a different way than Group 2.

- The carbonates ( $\text{M}_2\text{CO}_3$ ) are highly stable to heat.
- With increase of electropositive character from Li to Cs, the stability of these salts increases.
- Their nitrates decompose on strong heating to the corresponding nitrite and  $\text{O}_2$ .



- The  $\text{LiNO}_3$  decomposes completely to give corresponding oxide,  $\text{NO}_2$  and  $\text{O}_2$ .



THE EFFECT OF HEAT ON THE GROUP 2 CARBONATES

- All carbonates decompose on heating at appropriate temperature evolving  $\text{CO}_2$



- The values of the decomposition temperatures of these carbonates as given below:

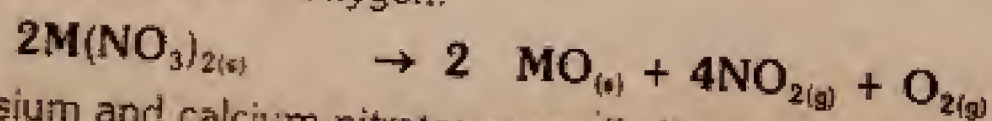
$$\text{BeCO}_3 = 25^\circ\text{C}, \quad \text{MgCO}_3 = 540^\circ\text{C}, \quad \text{CaCO}_3 = 900^\circ\text{C},$$

$$\text{SrCO}_3 = 1290^\circ\text{C}, \quad \text{BaCO}_3 = 1360^\circ\text{C}$$

Thus ease of decomposition decreases down the group

THE EFFECT OF HEAT ON THE GROUP 2 NITRATES

- All nitrates of Group 2 metals undergo thermal decomposition to give the metal oxide, nitrogen dioxide and oxygen.
- The nitrates are white solids, and the oxides produced are also white solids. Brown nitrogen dioxide gas is given off together with oxygen.



- Magnesium and calcium nitrates normally have water of crystallisation. So, the solid may dissolve in its own water of crystallisation to make a colourless solution before it starts to decompose.



(vii) Explain with examples that Beryllium hydroxide is Amphoteric?

An amphoteric oxide shows both acidic and basic properties, e.g. BeO  
It reacts with acids to form salts



It also reacts with bases to form salts



Reducing agent  
is an element that  
loses (donate) an electron  
to another. The reducing  
agent is losing  
electron, it is said  
to be oxidized.  
That removes  
an electron from  
another species -  
e

(viii) Explain the trends in oxidation states with suitable examples.

See Page 38

(ix) Discuss the inert pair effect in the:

(a) formation of ionic bonds (b) formation of covalent bonds

See Page 39

(x) Discuss in detail acid-base trend in group 4 oxides.

See Page 43

(xi) Explain in detail the trends in group 7 of following physical properties.

(a) Electronegativity (b) Electron affinity

See Page 45

(xii)(a) Why is the bond enthalpy of F-F less as compared to Cl-Cl and Br-Br?

- It is due to very small F-F bond length than other X-X bond lengths. So due to short distance, the F atoms in  $\text{F}_2$  molecule repel each other and thus the dissociation of  $\text{F}_2$  molecule into F atoms becomes easy.
- X-X bond in  $\text{Cl}_2$  and  $\text{Br}_2$  molecules is stronger than F-F bond in  $\text{F}_2$  molecule. It is due to the possibility of the formation of multiple bonds in X-X bond with d-orbitals.

Hence bond enthalpy of F-F bond is less as compared to Cl-Cl and Br-Br bonds.

(b) Explain the order  $\text{F} > \text{Cl} > \text{Br} > \text{I}$  with respect to oxidizing agent/power.

The oxidizing power of halogens depends upon dissociation energy, electron affinity and hydration energy. The net energy released from all these process decreases down the group. Thus, formation of  $\text{F}^-$  ion releases most energy while formation of  $\text{I}^-$  ion releases least energy. It means that fluorine will take up electrons readily to form  $\text{F}^-$  ions. Thus,  $\text{F}_2$  will have highest oxidizing power among halogens. Similarly,  $\text{I}_2$  will have least oxidizing power among halogens.

Hence, the order of oxidizing power is  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$  (weakest oxidizing agents).

(xiii)(a) Why is fluorine much stronger oxidizing agent than chlorine?

It is because.

- The bond dissociation energy of fluorine is quite low, so it will dissociates rapidly to take up electron.
- The other factor is hydration energy. The  $\text{F}^-$  ion has high hydration energy due to small size, so it will form readily in solution. Thus fluorine will take up electrons readily to form  $\text{F}^-$  ions than chlorine. Hence, fluorine is a much stronger oxidizing agent than chlorine.

H F's dissociation is

(b) HCl is strong acid as compared to HF. Why?

In HF, molecules are Hydrogen-bonded in a zigzag manner. Thus, H is entrapped between two F atoms as shown in the fig. Moreover, the bond energy of H-F bond is considerably greater than H-I bond. Thus, HF cannot donate its  $\text{H}^+$  ions easily, hence it is a weaker acid.

highest,  $\text{H}^+$ ,  $\text{F}^-$

F<sup>-</sup> ion





**TEST YOUR SKILLS**

**Marks: 85**

**OBJECTIVE**

**Marks: 17**

Time: 25 Minutes

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks.

- (i) In a group the atomic radius increase due to successive increase of  
(A) electronic shells (B) proton shells (C) neutron shells (D) nucleus
- (ii) Green is characteristic flame colour of  
(A) calcium (B) barium (C) strontium (D) sodium
- (iii) The flame colour of sodium metal or its compounds is  
(A) bright crimson (B) violet (C) golden yellow (D) bright blue
- (iv) Due to small size of  $Be^{+2}$  ion, the oxide of BeO is  
(A) ionic (B) coordinate (C) covalent (D) none of these
- (v) Sulphur dioxide is fairly soluble in water, reacting with it to give solution of  
(A)  $H_2SO_4$  (B)  $H_2SO_3$  (C)  $H_2SO$  (D)  $NaHSO_3$
- (vi)  $Al_2O_3$  is  
(A) Amphoheric oxide (B) Acid oxide (C) basic oxide (D) both a and b
- (vii) Peroxides of alkali metals on reaction with ice cold water produce  
(A) metal oxide (B) metal hydroxide (C) metal (D) superoxide
- (viii) Highest electron affinity is shown by  
(A)  $F_2$  (B)  $I_2$  (C)  $Br_2$  (D)  $Cl_2$
- (ix) Reducing powers of halide ions ..... from  $I^-$  for  $Br^-$   
(A) increases (B) decreases (C) remain same (D) none of these
- (x) The increasing strength of halogens as oxidizing agents is  
(A)  $I_2 > Br_2 > Cl_2 > F_2$  (B)  $F_2 < Cl_2 < Br_2 < I_2$  (C)  $F_2 > Cl_2 > Br_2 > I_2$  (D)  $Cl_2 > Br_2 > I_2 > F_2$
- (xi) All the carbonates, sulphates and phosphates of alkaline earth metals are ..... In water  
(A) Sparingly soluble (B) soluble (C) insoluble (D) less soluble
- (xii) Lead (II) chloride  $PbCl_2$  is  
(A) white solid (B) liquid (C) volatile compound (D) both b and c
- (xiii)  $Ge^{2+}$  compounds are  
(A) Reducing agents (B) Oxidizing agents (C) both a and b (D) none of these
- (xiv) Substance boiling at higher temperature among following is  
(A) HI (B) HF (C) HCl (D) HBr
- (xv) The reactivity of alkali metals generally increase from  
(A) top to bottom (B) bottom to top  
(C) remain same throughout the group (D) none of these
- (xvi) The carbonates of alkali metals are not affected by heat except  
(A)  $Li_2CO_3$  (B)  $Na_2CO_3$  (C)  $K_2CO_3$  (D)  $Rb_2CO_3$
- (xvii) The radioactive element in halogen group is  
(A) Radon (B) Radium (C) Astatine (D) Bromine

Time: 2:35 Hours

**SUBJECTIVE**

**Section - B (Marks 42) (14 × 3 = 42)**

Total Marks Section B and C: 68

- Q2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines.
- (i) Although Na and P are present in the same period yet their oxides are different in nature.  $Na_2O$  is basic while  $P_2O_5$  is acidic. Why? (03)
  - (ii) (a) Write down the reaction of Mg with cold and hot water. (02)  
(b) Draw the structure of ortho silicic acid. (01)
  - (iii) Discuss the metallic and non-metallic character of group & elements. (03)
  - (iv) How hydrolysis of tetrahalides takes place. (03)
  - (v)  $CO_2$  is a gas while  $SiO_2$  is a solid although C and Si belong to the same group. (03)
  - (vi) HF is a weak acid than HI. Why. (03)
  - (vii) (a) Show the amphoteric nature of BeO. (03)  
(b) Write down the names of product formed when  $S_2Cl_2$  react with water. (02)  
(01)



- (viii) The oxidizing power of  $F_2$  is greater than  $Cl_2$ . Why? (03)
- (ix) Discuss the general group trends of group I elements. (03)
- (x) How NaOH react with  $H_3PO_4$ ? (03)
- (xi) Discuss the behaviour of  $AlCl_3$ . (03)
- (xii) Explain why nitrates and carbonates of Li are not stable. (03)
- (xiii) Differentiate the behaviour of Li and Na with amphoteric oxygen. (03)
- (xiv) Explain why solubility of alkaline earth metal carbonates decrease down the groups? (03)
- (xv) Why do the group I metals show strong electropositive character. (03)
- (xvi) Why normal oxides of alkali metals are not formed by the direct combination of metal and  $O_2$ ? (03)
- (xvii) Explain the trend of density in alkali metals. (03)
- (xviii) On what factors does the oxidizing power of halogen depends. (03)
- (xix) Why different colours are imparted by the atoms of the group & metals to the flame. (03)

### Section - C

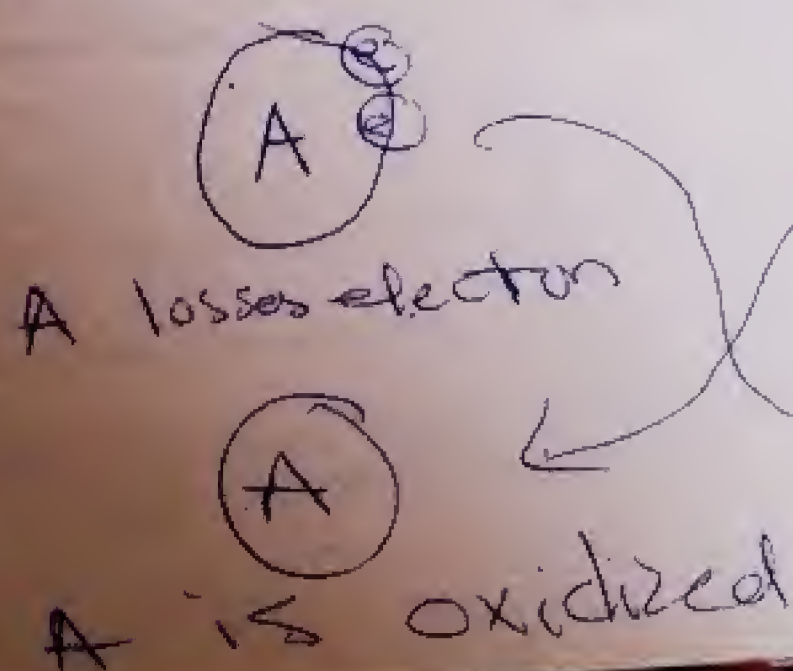
Note: Attempt any TWO questions. All questions carry equal marks. ( $2 \times 13 = 26$ )

- Q1. Discuss the metallic oxides and silicon dioxide under the following headings. (04)
- (a) Structures. (05)
- (b) Melting and Boiling Points. (04)
- (c) Electrical conductivity. (03)
- Q2. (a) Why is fluorine much stronger oxidizing agent than chlorine. (03)
- (b) HCl is strong acid as compared to Hf. Why. (3.5)
- (c) Explain the trends in detail of group I. (3.5)
- (i) Electronegativity (03)
- (ii) Electron affinity (03)
- Q3. (a) The pattern of first ionization energy and melting and boiling point is not smooth. Justify it. (03)
- (b) Why atomic radius increases in group and decreases along the period. (04)
- (c) Describe the trends in reaction of period 3 elements with water. (03)
- (d) Why Beryllium chloride covalent and not ionic.

Reducing agent

- \* reduces other substances and loses electron;
- \* oxidation state increases
- \* electron donor
- \*  $H_2, CO, Fe, Zn, Li, X$

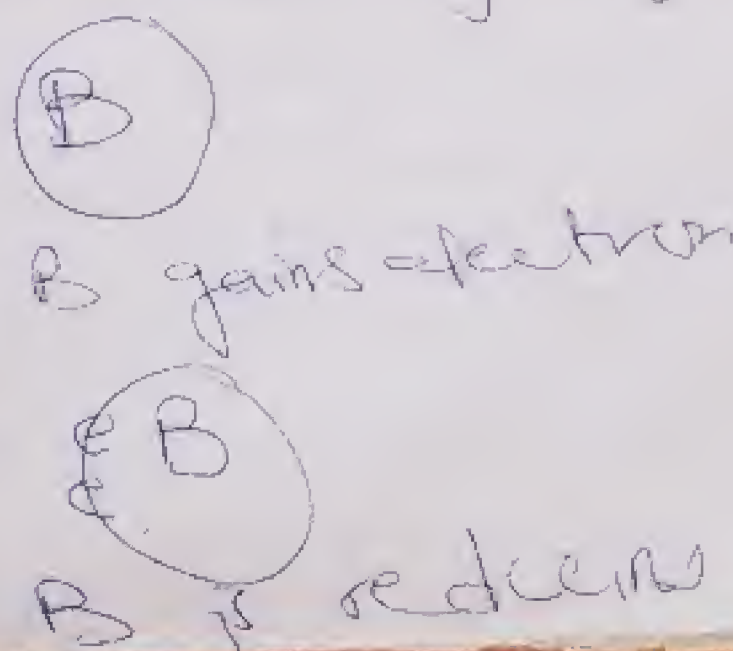
Reducing agent



oxidizing agent

- \* gains electron
- \* higher possible oxidation states, it will gain electron
- \* electron acceptor
- \*  $O_2, O_3, F_2, Br_2, H_2SO_4$ , Alkali

oxidizing agent





## CHAPTER # 14

# d and f-Block Elements: TRANSITION ELEMENTS

## INTRODUCTION

### Definition

The elements which have partially filled d or f-orbital either in their atomic states or in other common oxidation states are called transition elements.

- They are called d-block or f-block elements.
- d-block elements are called outer transition elements and f-block elements are called inner transition elements.

### Why are they called transition elements?

- They are called transition elements because they show transition in properties between s- and p-block elements.
- Thus there is a transition between highly reactive and strongly electropositive elements of s-block which form ionic bonds on one side and p-block elements which form covalent compounds on other side.

### Series of Transition Elements:

The d-block elements consist of following three series of ten elements each:

- (1) **3d-Series:** From Scandium (Sc=21) to Zinc (Zn=30)
- (2) **4d-Series:** From Yttrium (Y=39) to Cadmium (Cd=48)
- (3) **5d-Series:** From Lanthanum (La=57) to Mercury (Hg=80) [Lanthanide series (rare-earths) excluded]

The f-block elements constitute two series which are:

- (1) **4f-Series:** From Cerium (Ce = 58) to Lutetium (Lu = 71)
- (2) **5f-Series:** From Actinium (Ac = 89) to Lawrentium (Lr = 103) which are called actinides.

### General outermost configurations:

- (1) d-block elements =  $(n-1)d^{1-10} ns^2$
- (2) f-block elements =  $(n-1)d^1 (n-2)f^{1-14} ns^2$

### Remember!

The electronic configuration of  $_{25}\text{Mn}$  is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$  or  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$ . So, the valence subshell is  $4s^2$  i.e.  $ns^2$ , then d-subshell is  $3d^5$  i.e.  $(n-1)d^5$ . Thus, coefficient of d-subshell is one number less than the s-subshell. So, the general configuration is  $(n-1)d^{1-10} ns^2$ . The  $d^{1-10}$  means 1 to 10 electrons may be present. Similarly, for f-block, the d-subshell is one number less but the f-subshell is two numbers less than the s-subshell. Thus, their general configuration is  $(n-1)d^1 (n-2)f^{1-14} ns^2$ .

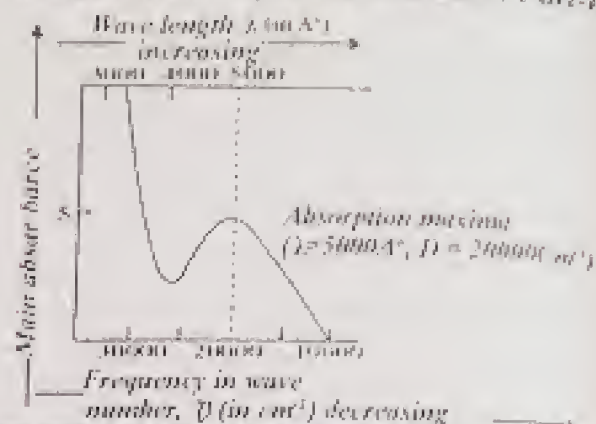
### Why is Zn-group included in Transition elements?

Zn, Cd and Hg are not regarded as transition elements because they have completely filled d-orbitals. However, they are included in transition elements because they form complexes with ammonia, halide ions and amines and their chemical behaviors is similar to transition elements.

### Coinage metals are transition elements. Justify the statement.

Coinage metals are Cu, Ag, Au. They are transition elements since  $\text{Cu}^{2+}$  has  $3d^9$  configuration,  $\text{Ag}^{2+}$  has a  $4d^9$  and  $\text{Au}^{3+}$  has  $5d^8$  configurations. Although all these metals have  $d^{10}$  configurations in atomic states.

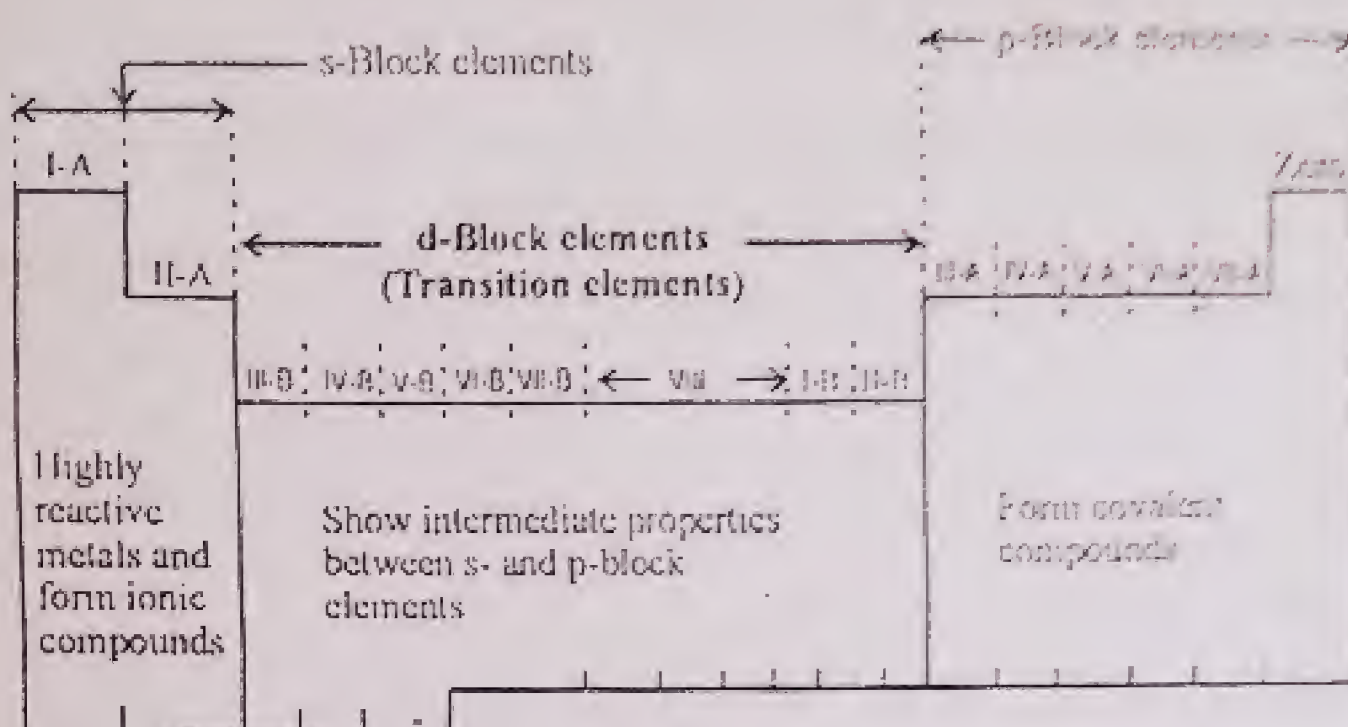
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### Position of d-block elements in the periodic table

Following diagram show the position of d-block elements in the periodic table

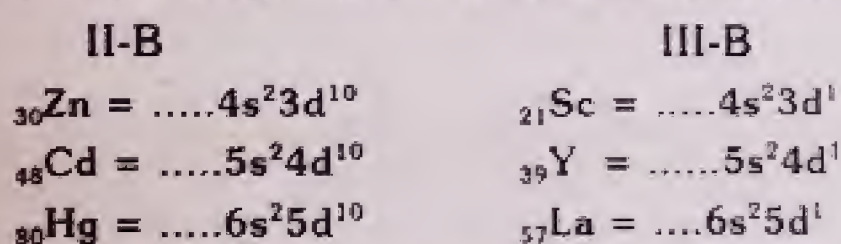


Position of d-block elements in the periodic table

Exercise Q3(i) (b) What are typical and non-typical transition elements?

#### Typical and non-Typical Transition Elements:

The elements of the group II-B and III-B have the electronic distribution as follows



- It is clear that the elements of II-B i.e. Zn, Cd and Hg do not have partially filled d-subshell in the elemental state or ionic state. They do not show the typical properties of the transition elements to an appreciable extent.
- The elements of the group III-B are  $_{21}\text{Sc}$ ,  $_{39}\text{Y}$  and  $_{57}\text{La}$ . They do not show many of their properties typical of transition elements. In the compound state, they show tri-positive ion i.e.  $\text{Sc}^{+3}$ ,  $\text{Y}^{+3}$  and  $\text{La}^{+3}$ . In this way they do not have any electron in d-orbital.

For these reasons, the elements of group II-B and III-B are non-typical transition elements

Non-Typical Transition Elements	Typical Transition Elements
II-B and III-B	IV-B, V-B, VI-B, VII-B, VIII-B and I-B

## GENERAL FEATURES

### GENERAL FEATURES OF TRANSITION ELEMENTS

- They are all metallic in nature.
- Some of the transition elements play an important role in the industry. These metals are Ti, Cr, Fe, Ni, Co, Mn, W, Zr, Nb, Ta and Th etc.
- They are all hard and strong metal with high melting and boiling points. They are good conductors of heat and electricity.
- They form alloys with one another and other elements of periodic table as well.
- With a few exceptions, they show variable oxidation states.
- Their ions and compounds are colored in the solid state and the solution state.



## QUICK QUIZ-1

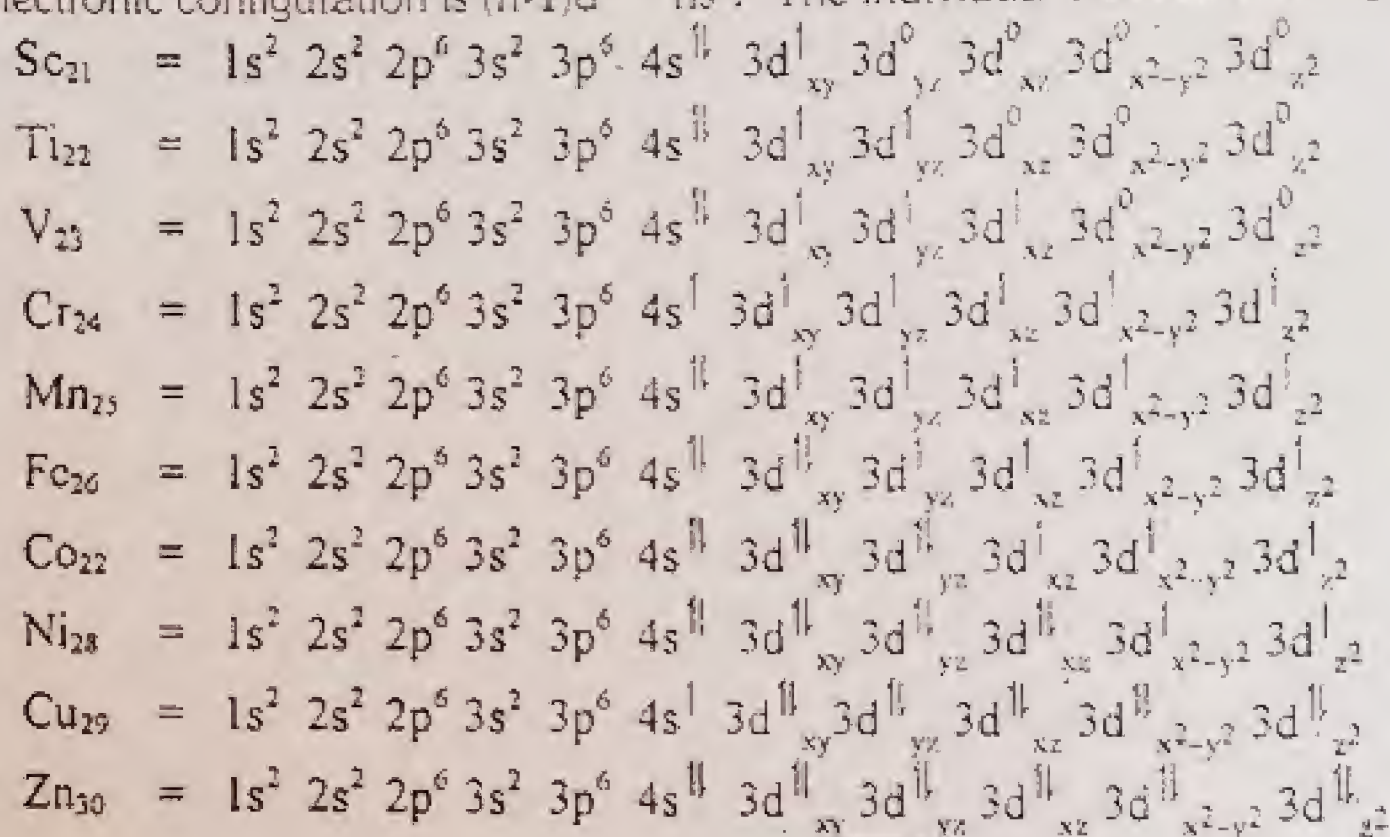
(1) Give the electronic configuration of the elements of first transition series.

First Transition series is 3d-series. It includes 10 elements from  $_{21}\text{Sc}$  to  $_{30}\text{Zn}$ .

(The electronic configuration is given below on the next page.)

(2) Write the general state electronic configuration (s, p, d, f) of the elements of the first transition series (z=21 to 30) indicating the number of unpaired electrons in each case.

The general state electronic configuration is  $(n-1)d^{1-10}ns^2$ . The individual electronic configuration of elements are:



(3) Give the names, symbols and electronic configuration of the elements of second transition series.

The second transition series is 4d-series. It includes 10 elements from  $_{39}\text{Y}$  to  $_{48}\text{Cd}$ . The electronic configuration of 4-d series elements is:

4d-Series Transition Elements		
Elements Symbol	Name	Electronic configuration
$_{39}\text{Y}$	Yttrium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^1$
$_{40}\text{Zr}$	Zirconium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$
$_{41}\text{Nb}$	Niobium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^3$
$_{42}\text{Mo}$	Molybdenum	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1 4d^5$
$_{43}\text{Tc}$	Technetium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^5$
$_{44}\text{Ru}$	Ruthenium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^6$
$_{45}\text{Rh}$	Rhodium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^7$
$_{46}\text{Pd}$	Palladium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^8$
$_{47}\text{Ag}$	Argentum (Silver)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1 4d^{10}$
$_{48}\text{Cd}$	Cadmium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10}$

(4) Discuss the trends and variation in oxidation states (valency) of transition metals.

See Page 70

(5) Explain the magnetic properties of transition metals.

See Page 71

(6) What do you understand by diamagnetism and paramagnetism.

See Page 71

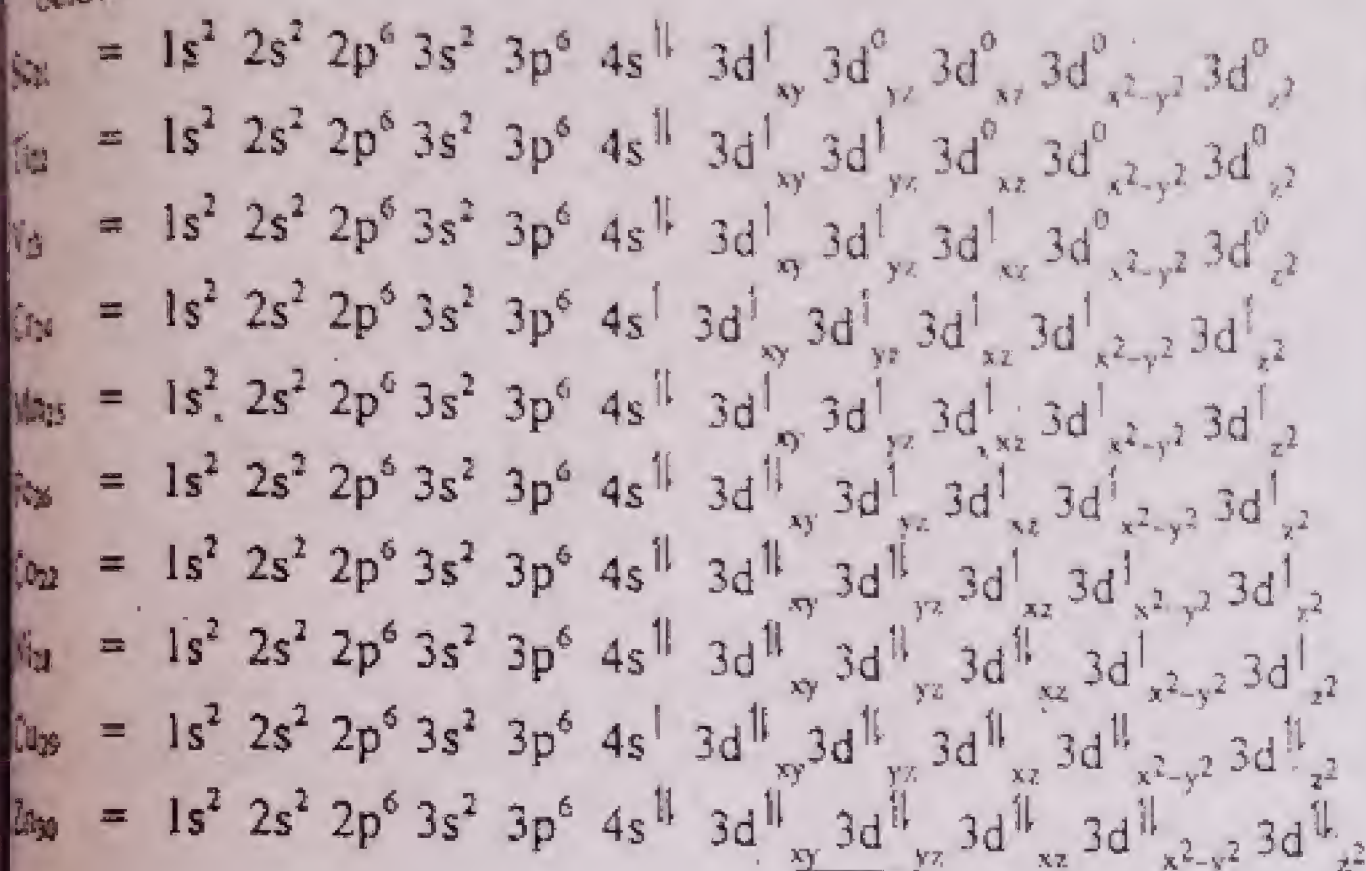


Exercise Q3(i)(a): What is the valence shell configuration of transition elements?

How does it affect the following properties? (i) Binding energy (ii) Paramagnetism (iii) oxidation states

## ELECTRONIC STRUCTURE

Electronic distribution of first series of transition elements and the detailed valence shell configuration is given below.



		3d					4s
Sc (Ar)		↑					↑
Ti (Ar)		↑	↑				↑
V (Ar)		↑	↑	↑			↑
Cr (Ar)		↑	↑	↑	↑	↑	↑
Mn (Ar)		↑	↑	↑	↑	↑	↑
Fe (Ar)		↑	↑	↑	↑	↑	↑
Co (Ar)		↑	↑	↑	↑	↑	↑
Ni (Ar)		↑	↑	↑	↑	↑	↑
Cu (Ar)		↑	↑	↑	↑	↑	↑
Zn (Ar)		↑	↑	↑	↑	↑	↑

## ELECTRONIC DISTRIBUTION OF 4d AND 5d-SERIES:

- The following table shows the electronic distribution of 4d and 5d-block elements.
- The elements of the group number VI-B, i.e. Cr group shows the same abnormality except  $_{74}\text{W}$ .
- Similarly, the elements of the group I-B that is Cu-family also show the abnormal distribution.
- Following table shows the electronic distribution of 3d, 4d, 5d series

3d-block elements		4d-block elements		5d-block elements	
Elements	Electronic configuration	Elements	Electronic configuration	Elements	Electronic configuration
Sc (21)	[Ar] $3d^1 4s^2$	Y (39)	[Kr] $4d^1 5s^2$	La (57)	[Xe] $5d^1 6s^2$
Ti (22)	[Ar] $3d^2 4s^2$	Zr (40)	[Kr] $4d^2 5s^2$	Hf (72)	[Xe] $4f^{14} 5d^2 6s^2$
V (23)	[Ar] $3d^3 4s^2$	Nb (41)	[Kr] $4d^4 5s^1$	Ta (73)	[Xe] $4f^{14} 5d^3 6s^2$
Cr (24)	[Ar] $3d^5 4s^1$	Mo (42)	[Kr] $4d^5 5s^1$	W (74)	[Xe] $4f^{14} 5d^4 6s^2$
Mn (25)	[Ar] $3d^5 4s^2$	Tc (43)	[Kr] $4d^5 5s^2$	Re (75)	[Xe] $4f^{14} 5d^5 6s^2$
Fe (26)	[Ar] $3d^6 4s^2$	Ru (44)	[Kr] $4d^7 5s^1$	Os (76)	[Xe] $4f^{14} 5d^6 6s^2$
Co (27)	[Ar] $3d^7 4s^2$	Rh (45)	[Kr] $4d^8 5s^1$	Ir (77)	[Xe] $4f^{14} 5d^7 6s^2$
Ni (28)	[Ar] $3d^8 4s^2$	Pd (46)	[Kr] $4d^{10}$	Pt (78)	[Xe] $4f^{14} 5d^9 6s^1$
Cu (29)	[Ar] $3d^{10} 4s^1$	Ag (47)	[Kr] $4d^{10} 5s^1$	Au (79)	[Xe] $4f^{14} 5d^{10} 6s^1$
Zn (30)	[Ar] $3d^{10} 4s^2$	Cd (48)	[Kr] $4d^{10} 5s^2$	Hg (80)	[Xe] $4f^{14} 5d^{10} 6s^2$



**Exercise Q3(i)(a):** What is the valence shell configuration of transition elements?  
 For this see above page 69  
 How does it affect the following properties?  
 (i) Binding energy (ii) Paramagnetism (iii) oxidation states

## BINDING ENERGY

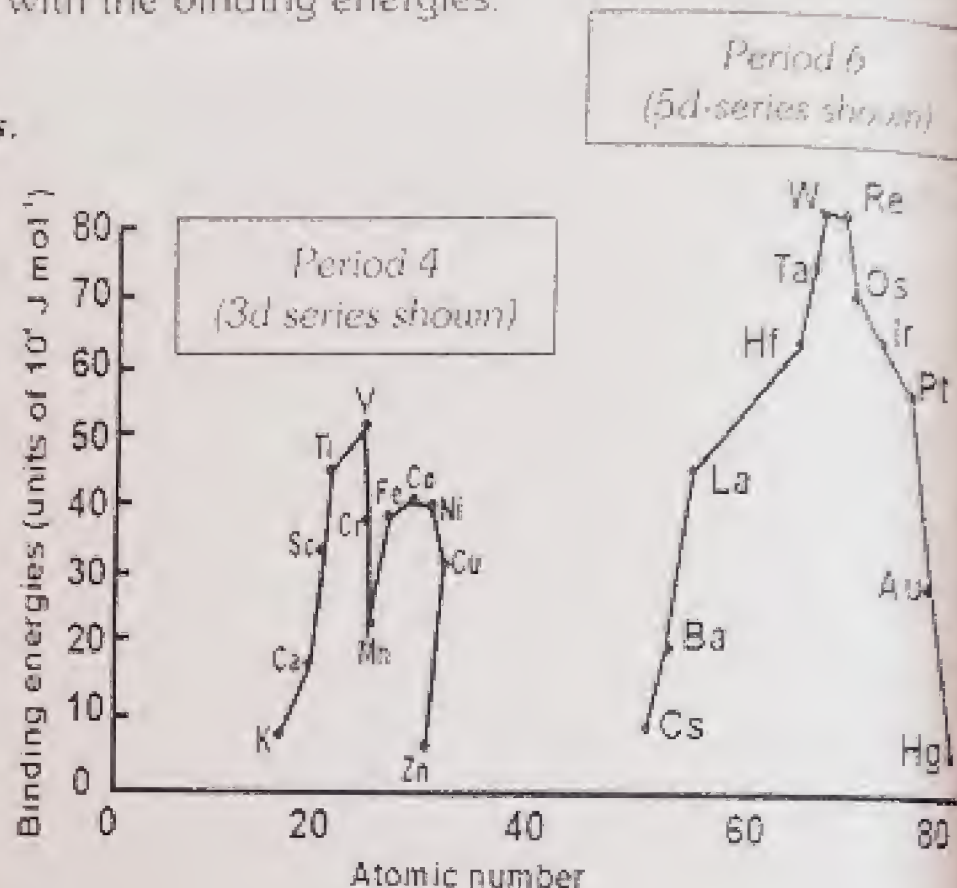
- The mechanical properties of transition elements are related with the binding energies.
- Transition elements are tough, malleable and ductile.

**The toughness of the metals is due to greater binding energies.**

It is because the s-electron of outermost shell takes part in chemical bonding. However, the electrons of half-filled d-orbitals also participate in bonding. So, they have greater binding energies and toughness.

### Variation in binding energies:

- The number of unpaired electrons increases up to group V-B from left to the right in any d-block series. i.e., up to V family (group V-B or group 5) or Cr family (group VI-B or group 6).
- After that the pairing of electron starts.
- The unpaired electrons become zero at **group II-B**.
- It means that binding forces go on increasing up to Cr and then decrease after that. This is shown for the elements of 3d and 5d series in the figure.



**Quick Quiz-1 (4):** Discuss the trends and variation in oxidation states (valency) of transition metals.

## VARIABLE OXIDATION STATES

- Transition elements are electropositive, so they have positive oxidation states.
- All 3d series elements show an oxidation state of +2 in addition to higher oxidation states when the electrons of 4s-orbital take part in bonding.
- Transition elements show variable oxidation states.** The reason is that they have d-electrons in addition to s-electron for bond formation. These elements have several (n-1) d and ns electrons. The energies of (n-1) d and ns orbitals are very close to each other. The (n-1) d electrons are as easily lost as ns electrons.
- In the highest oxidation states of first five elements, all s and d-electrons are used for bonding.
- Among the 3d series, Mn has maximum oxidation states, and goes up to +7.
- The oxidation numbers +2 and +3 are more common.
- Positive oxidation states increase up to the middle of series and after that they decrease.** It is because the number of unpaired electrons increases up to the middle and then decreases.

			3d	4s	Oxidation states
Sc	[Ar]	3d <sup>1</sup> 4s <sup>2</sup>	1	1↓	2 3
Ti	[Ar]	3d <sup>2</sup> 4s <sup>2</sup>	1 1	1↓	2 3 4
V	[Ar]	3d <sup>3</sup> 4s <sup>2</sup>	1 1 1	1↓	2 3 4 5
Cr	[Ar]	3d <sup>5</sup> 4s <sup>1</sup>	1 1 1 1 1	1	2 3 4 5 6
Mn	[Ar]	3d <sup>5</sup> 4s <sup>2</sup>	1 1 1 1 1	1↓	1 2 3 4 5 6 7
Fe	[Ar]	3d <sup>6</sup> 4s <sup>2</sup>	1↓ 1 1 1 1	1↓	1 2 3 4 5 6
Co	[Ar]	3d <sup>7</sup> 4s <sup>2</sup>	1↓ 1↓ 1 1 1	1↓	2 3 4 5
Ni	[Ar]	3d <sup>8</sup> 4s <sup>2</sup>	1↓ 1↓ 1↓ 1 1	1↓	2 3 4
Cu	[Ar]	3d <sup>10</sup> 4s <sup>1</sup>	1↓ 1↓ 1↓ 1↓ 1↓	1	1 2 3
Zn	[Ar]	3d <sup>10</sup> 4s <sup>2</sup>	1↓ 1↓ 1↓ 1↓ 1↓	1↓	2



Block Quiz-1 (5): Explain the magnetic properties of transition metals.

Block Quiz-1 (6): What do you understand by diamagnetism and paramagnetism.

## MAGNETIC BEHAVIOUR

### Paramagnetism

The compounds attracted into the magnetic field are called paramagnetic and the phenomenon is called paramagnetism.

Many transition elements and their compounds are paramagnetic.

Paramagnetism is due to the unpaired electrons present in the metals and their compounds.

Examples:  $Mn^{+2}$ ,  $Fe^{+2}$  etc.

### Diamagnetism

The compounds which are slightly repelled by magnetic field are called diamagnetic and the phenomenon is called diamagnetism.

Some substances in which even number of electrons are present, and have paired spins are diamagnetic.

Examples:  $Zn^{+2}$ ,  $Sc^{+3}$  etc.

### Ferromagnetism

The substances which can be magnetized are called ferromagnetic and the phenomenon is called ferromagnetism.

e.g., Fe, Co and Ni are ferromagnetic.

### Magnetic moment

The magnetic moment ( $\mu$ ) is related to the number of unpaired electrons ( $n$ ) by the equation:

$$\mu = \sqrt{n(n+2)} \text{ , where } n = \text{number of unpaired electrons in a substance.}$$

It is measured in Bohr magneton. Its symbol is  $\mu_B$ .

By measuring magnetic moment, the nature of transition metal compound and oxidation state of transition metal can be calculated.

Exercise Q3(I) (c) Explain catalytic Activity of transition elements.

## CATALYTIC ACTIVITY

Most of the transition elements are used as catalysts. The compounds of transition metals are also catalysts.

It is due to following reasons

- The reason is that the transition metals show variety of oxidation states. In this way, they can form intermediate products with various reactants.
- They also form interstitial compounds which can absorb an activator to the reacting species.

Some of the important examples of catalysts are as follows:

- (1) A mixture of  $ZnO$  and  $Cr_2O_3$  is used for the manufacture of methyl alcohol.
- (2)  $Ni$ ,  $Pt$  and  $Pd$  are catalysts for the hydrogenation of vegetable oil and saturation of alkenes and alkynes to alkanes.
- (3)  $MnO_2$  can be used as a catalyst for the decomposition of  $H_2O_2$ .
- (4)  $TiCl_4$  is used as catalyst for the manufacture of plastics.
- (5)  $V_2O_5$  is used to oxidize  $SO_2$  to  $SO_3$  in the manufacture of  $H_2SO_4$ .
- (6)  $Fe$  is used as a catalyst for synthesis of  $NH_3$  in Haber's process about 1% of  $Na_2O$  or  $K_2O$  and about 1%  $SiO_2$  or  $Al_2O_3$  are added as promoters.  $Mo$  is also sometimes used as a promoter.



## ALLOY FORMATION

- Alloy is mixture of two or more than two metals.
- Transition metals form alloys with each other. It is because transition elements have almost similar sizes and atoms of the one metal can easily take up positions in crystal lattice of the other. Thus, they form substitutional alloys among themselves.

### Example:

- Alloy steels are the materials in which the iron atoms are substituted by Cr, Mn and Ni. Steel has more useful properties than iron.
- Brass, bronze and coinage alloys are the best alloys.

### Properties:

As alloys are prepared according to the requirements, their characteristics are different. However, few properties are common which are as follows:

- Alloys are comparatively cheap.
- They are strong and flexible but hard alloys can also be prepared.
- They have long life because they do not corrode.
- They are durable.
- They have high melting points.
- They are better conductor but non-conductor alloys are also prepared.

**Exercise Q3(i) (d) Write composition, properties and uses of: Brass, Bronze and Nichrome alloys.**

Alloys of Metals	Composition	Properties and Uses
Brass	Cu = 60 - 80 % Zn = 20 - 40 %	<ul style="list-style-type: none"> <li>It is a strong alloy of copper which is soft and flexible.</li> <li>It does not corrode.</li> <li>Due to low melting point, it is easy to use.</li> <li>It is used to make locks, keys, water taps, pipes, artificial jewellery, door handles and parts of machines.</li> </ul>
Bronze	Cu = 90 - 95 % Sn = 5 - 10 %	<ul style="list-style-type: none"> <li>It is strong, brilliant and long lasting.</li> <li>It does not corrode.</li> <li>It is used to prepare medals, coins, badges and bullets etc.</li> <li>Besides these, decorative articles are also made from this alloy.</li> </ul>
Nichrome		It is used in electric heaters and filaments of furnaces.

## QUICK QUIZ-2:

### (1) How magnetic moment is measured

- Theoretically, the magnetic moment ( $\mu$ ) is related to the number of unpaired electrons ( $n$ ) by the equation:  

$$\mu = \sqrt{n(n+2)}$$
, where  $n$  = number of unpaired electrons in a substance.
- Experimentally, the magnetic moment of compounds is generally measured by Guoy balance method.

### (2) Give unit of magnetic moment

The magnetic moment is measured in the units of Bohr Magneton. Its symbol is  $\mu_B$ .

### (3) Give difference between nichrome and bronze

Both these are alloys.

The nichrome alloy consists of Ni = 60 %, Cr = 15 % and Fe = 25 %

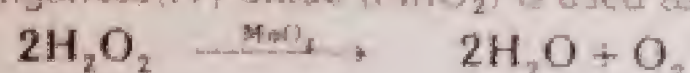
The Bronze alloy consists of Cu = 90 - 95 % and Sn = 5 - 10 %.



Q Name the catalyst use for

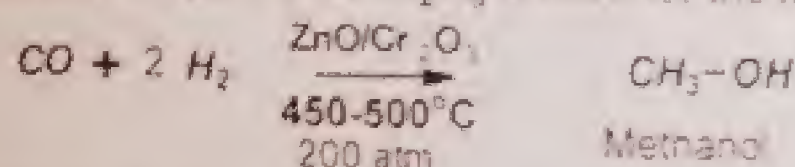
(i) Decomposition of  $H_2O_2$

Manganese(IV) oxide ( $MnO_2$ ) is used as a catalyst for the decomposition of  $H_2O_2$ . The reaction is



(ii) Manufacturing of  $CH_3OH$

A mixture of  $ZnO$  and  $Cr_2O_3$  is used for the manufacture of methyl alcohol. The reaction is



Q On which factor binding energy depends

The binding energy depends upon the number of unpaired electrons. Generally, greater the number of unpaired electrons, greater is the binding energy. e.g. In 3d-series of transition metals, the number of unpaired electrons increases up to the middle and then decreases onward. Thus, binding energy also increases up to the middle and then decreases onward.

Q Why transition element shows variable oxidation state.

They show variable oxidation state because they have d-electrons in addition to s-electron for bond formation. These elements have several (n-1) d and ns electrons. The energies of (n-1) d and ns orbitals are very close to each other. The (n-1) d electrons are as easily lost as ns electrons. Thus, they show variable oxidation states.

Q Which property of transition elements enable them to serve as catalyst

It is due to following reasons

- The reason is that the transition metals show variety of oxidation states. In this way, they can form intermediate products with various reactants.
- They also form interstitial compounds which can absorb an activator to the reacting species.

Q Why alloys are prepared?

Alloys are prepared due to several desirable properties. e.g.

- Alloys are comparatively cheap.
- They are strong and flexible but hard alloys can also be prepared.
- They have long life because they do not corrode.
- They have high melting points.

## COORDINATION COMPOUNDS

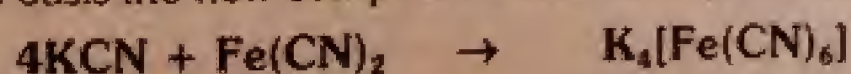
Definition:

Those compounds which contain complex molecules or complex ions capable of independent existence are called coordination compounds or complex compounds.

Such compounds are formed by the coordination of an electron pair donor to metal atom or an ion.

Explanation:

- Let two substances are mixed together, i.e.,  $KCN$  and  $Fe(CN)_2$ .
- When this mixture is evaporated, a new compound is obtained.
- This compound when dissolved in water ionizes into  $K^+$  and  $[Fe(CN)_6]^{4-}$ .
- On this basis the new compounds has been given the formula  $K_4[Fe(CN)_6]$ .



$[Fe(CN)_6]^{4-}$  is called complex ion.



**PARTS OF COMPLEX COMPOUND AFTER DISSOCIATION IN A SOLVENT:**

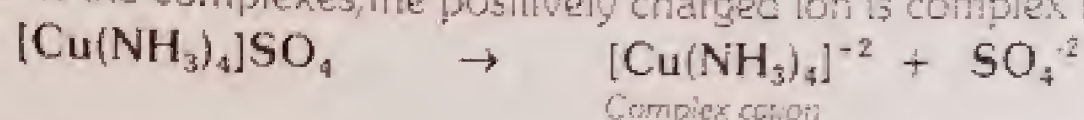
A complex compound is mostly made up of two parts:

- (1) Positively charged ion or cation.
- (2) Negatively charged ion or anion.

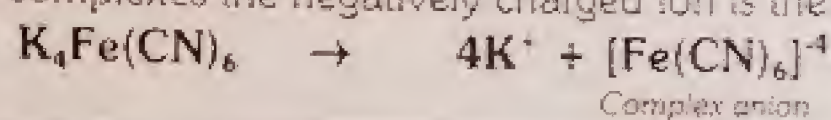
e.g. in  $K_4Fe(CN)_6$ ,  $K^+$  is a cation and  $[Fe(CN)_6]^{4-}$  is the anion.

**Complex ion as Cation:**

In some of the complexes, the positively charged ion is complex ion

**Complex ion as Anion:**

In some of the complexes the negatively charged ion is the complex ion

**COMPONENTS OF COMPLEX COMPOUNDS**

Complex compound consist of three components

1. A positively or negatively charged ion which is not complex.
2. A central metal atom or ion which is consisted of transition element.
3. Electron pair donor which is negatively charged, positively charged or neutral.

**(A) CENTRAL METAL ATOM OR ION**

A metal atom or ion is usually a transition element. It is surrounded by a number of ligands.

Examples:

- (1) In  $K_4[Fe(CN)_6]$ ,  $Fe^{+2}$  is the central metal ion. Six ligands ( $CN^-$  ions) are surrounding it.
- (2) In  $K_3[Fe(CN)_6]$ ,  $Fe^{+3}$  is the central metal ion. Six ligands ( $CN^-$  ions) are surrounding it.
- (3) In  $[Cu(NH_3)_4]SO_4$ ,  $Cu^{+2}$  is the central metal ion. Four ligands ( $NH_3$  ions) are surrounding it.
- (4) In  $[Ag(NH_3)_2]Cl$ ,  $Ag^{+2}$  is the central metal ion. Two ligands ( $NH_3$ ) are surrounding it.

**Exercise Q3(ii) (a) Explain different types of ligand with examples**

**(B) LIGAND**

The atom, ion (usually anions) or neutral molecule which surrounds the central metal atom or ion by donating the electron pair is called ligand.

Examples:

- (1) In  $K_4[Fe(CN)_6]$  and  $K_3[Fe(CN)_6]$ ,  $CN^-$  is the ligand.
- (2) In  $[Cu(NH_3)_4]SO_4$  and  $[Ag(NH_3)_2]Cl$ ,  $NH_3$  is the ligand.

**TYPES OF LIGANDS:**

Depending upon number of donatable electron pairs, ligands are of many types:

**(1) Monodentate Ligands:**

Those ligands which have only one donatable electron pair. Such ligands may be negatively charged, or neutral.

Examples:

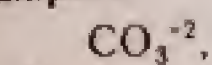
- (1) Negatively charged ligands  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $OH^-$ ,  $CN^-$
- (2) Neutral ligands  $H_2O$ ,  $NH_3$ ,  $CO$



**(2) Bidentate ligands:**

Those ligands which have two donatable electron pairs are called bidentate ligands.

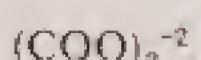
**Examples:**



Carbonate ion,



Sulphate ion,



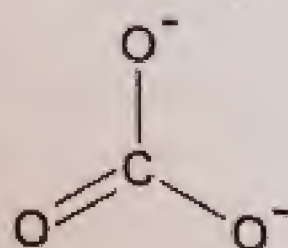
Oxalate ion,



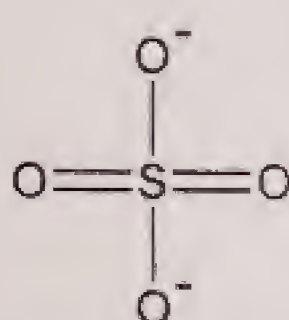
Hydrazine,



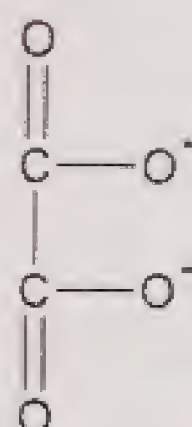
Ethylene diamine



carbonate ion



sulphate ion

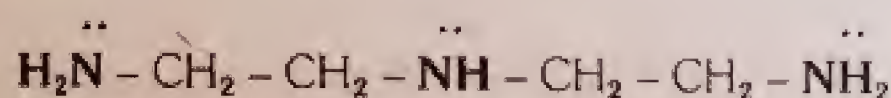


oxalate ion

**(3) Tridentate ligands:**

Those ligands which have three donatable electron pairs

**Example:**



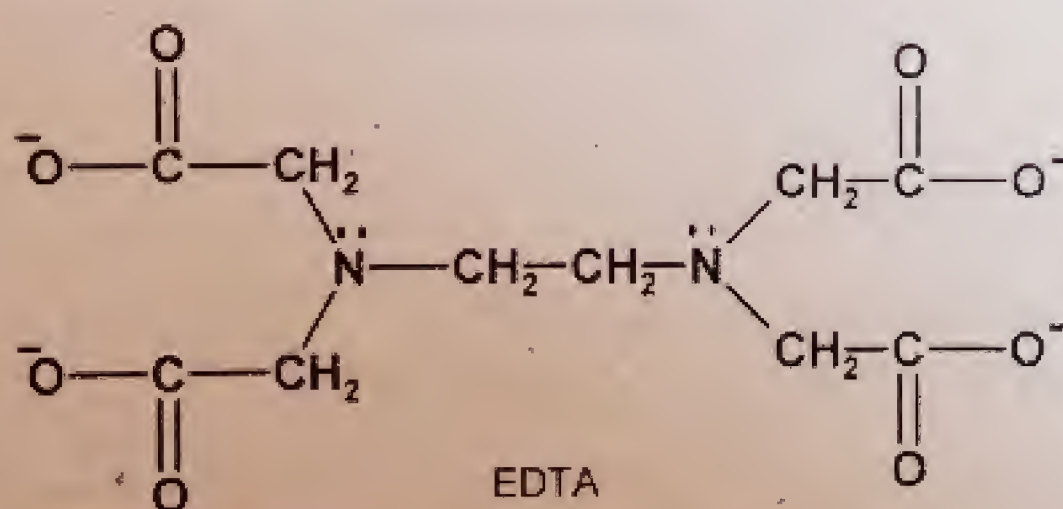
Diethylene triamine

**(4) Hexadentate ligands:**

Those ligands which have six donatable electron pairs.

**Example:**

Ethylenediaminetetracetate (EDTA)



EDTA

**(C) COORDINATION NUMBER OR LIGANCY:**

It is the total number of the atoms of the ligands that can coordinate to the central metal ion. Numerically coordination number represents the total number of the chemical bonds formed between the central metal ion and the donor atoms of the ligands.

**Examples:**

- (1) In  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , the coordination number of  $\text{Fe}^{+2}$  is six.
- (2) In  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ , the coordination number of  $\text{Cu}^{+2}$  is four
- (3) In  $[\text{Ag}(\text{NH}_3)_2]$ , the coordination number of  $\text{Ag}^+$  is two
- (4) In  $[\text{Ni}(\text{CO})_4]$ , the coordination number of  $\text{Ni}^0$  is four



**(D) COORDINATION SPHERE**

The central neutral atom or ion along with ligand is called coordination sphere. It is usually placed in the square brackets. It may be positively charged, negatively charged or neutral.

Examples:

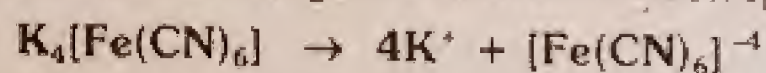
- (1) In  $K_4[Fe(CN)_6]$ , the ion  $[Fe(CN)_6]^{-4}$  is the coordination sphere of this complex compound
- (2) In  $[Cu(NH_3)_4]SO_4$ , the ion  $[Cu(NH_3)_4]^{+2}$  is the coordination sphere of this complex compound
- (3) In  $K_3[Fe(CN)_6]$ , the ion  $[Fe(CN)_6]^{-3}$  is the coordination sphere of this complex compound
- (4) In  $[Ag(NH_3)_2]Cl$ , the ion  $[Ag(NH_3)]^{+1}$  is the coordination sphere of this complex compound
- (5) In  $[Ni(CO)_4]$ , the ion  $[Ni(CO)_4]$  is the coordination sphere of this complex compound

**(E) CHARGE ON THE COORDINATION SPHERE**

It is the algebraic sum of charges present on the central metal ion and total charge on the ligands.

Example:

In  $K_4[Fe(CN)_6]$  the charge on the coordination sphere can be calculated as follows.



Since charge on each ligand is  $= -1$

Charge on  $6CN^-$   $= -6$

Charge on iron  $= +2$

So the charge on the coordination sphere  $= -6 + 2 = -4$

**NOMENCLATURE OF COMPLEX COMPOUNDS**

Exercise Q3(ii) (b) Describe the rules for naming the coordination complexes with examples.

Complex compounds are named according to following rules give by IUPAC

**(1) Order of Ions:**

Cations are named first and then the anions.

Examples:

In  $K_4[Fe(CN)_6]$ , we will call  $K^+$  first and then  $[Fe(CN)_6]^{-4}$

In  $[Cu(NH_3)_4]SO_4$ , we will call  $[Cu(NH_3)_4]^{+2}$  first and then  $SO_4^{-2}$ .

**(2) Naming of ligands:**

(i) The ligands which are negatively charged end in O. e.g.

Ligand	Name	Ligand	Name
$F^-$	Fluoro	$CN^-$	Cyno
$Cl^-$	Chloro	$CH_3COO^-$	Acetato
$Br^-$	Bromo	$C_2O_4^{-2}$	Oxalato
$I^-$	Iodo		

(ii) Neutral ligands are called as such. e.g.

Ligand	Name	Ligand	Name
$H_2O$	Aquo or Aqua	$CO$	Carbonyl
$NH_3$	Ammine	$NO$	Nitrosyl



(iii) Positively charged ligands end in "ium" e.g.

Ligand	Name	Ligand	Name
$\text{NH}_2\text{NH}_3^+$	Hydrazinium	$\text{NH}_4^+$	Ammonium
$\text{NO}^+$	Nitrosylium		

#### Order of ligands:

All ligands are arranged alphabetically without any preference order. The numerical prefixes (di, tri, etc.) are not considered.

#### More than one same type of ligands

The prefixes di for two, tri for three, tetra for four, penta for five and hexa for six are used in order to indicate more than one ligands, use

#### Termination of name of metal

If the complex ion is negatively charged then the name of the metal ends in "ate"  
e.g. In  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , the name is potassium hexacyanoferrate (II).

#### Oxidation number of metal ion

The oxidation number of the metal ion is represented by roman numeral in parenthesis written after the name of the metal.

#### More than one polydentate ligands

The number of polydentate ligands is indicated by bis for two, tris for three and tetrakis for four.

#### Examples:

(a) In the following complexes, the complex ion has negative charge. So, the name of the metal ends in ate.

- |   |                                       |
|---|---------------------------------------|
| (1) $\text{K}_4[\text{Fe}(\text{CN})_6]$            | Potassium hexacyanoferrate (II)       |
| (2) $\text{K}_3[\text{Fe}(\text{CN})_6]$            | Potassium hexacyanoferrate (III)      |
| (3) $\text{Na}[\text{Mn}(\text{CO})_5]$             | Sodium Pentacarbonylmanganate (-I)    |
| (4) $\text{K}_2[\text{PtCl}_6]$                     | Potassium hexachloroplatinate (IV)    |
| (5) $\text{Na}_2[\text{Ni}(\text{CN})_4]$           | Sodium tetracyanonickelate            |
| (6) $\text{Na}_2[\text{Fe}(\text{CN})_5 \text{NO}]$ | Sodium pentacyanonitrosylferrate(III) |
| (7) $(\text{NH}_4)_2[\text{PtCl}_6]$                | Ammonium hexachloroplatinate(IV)      |
| (8) $\text{K}_2[\text{Cu}(\text{CN})_4]$            | Potassium tetracyanocuprate(II)       |
| (9) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$        | Hexaaquocobalt(II) ion                |
| (10) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$       | Hexaquoiron(II) ion                   |
| (11) $\text{Na}_3[\text{CoF}_6]$                    | Sodium hexafluorocobaltate(III)       |

(b) In the following complexes the complex ion has positive charge. So the name of the metal is called as such:

- |  |  |
|--|--|
| (1) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$                | Hexaamminecobalt (III) chloride                  |
| (2) $[\text{Co}(\text{F})_6]\text{Cl}_3$                   | Hexafluorocobalt (III) chloride                  |
| (3) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$         | Hexaaquochromium (III) chloride                  |
| (4) $[\text{Co}(\text{en})_2]\text{Cl}_2$                  | Dichlorobisethylenediamminecobalt (III) chloride |
| (5) $(\text{PtCl}(\text{NO}_2)(\text{NH}_3)_4)\text{SO}_4$ | Tetraamminechloronitro platinum (IV) sulphate    |

"en" is the abbreviation of  
"ethylene diammine"

The formula is





- |  |   |
|--|---|
| (7) $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$            | Diamminesilver(I) chloride              |
| (8) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$          | Hexaamminecobalt(III) chloride          |
| (9) $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}$ | Tetraaquadichlorochromium(III) chloride |
| (10) $[\text{Ni}(\text{CN})_4]^{2-}$                 | Tetracyanonicklate(II) ion              |

(c) The following complexes are neutral. Therefore, they have ONE WORD name.

- |   |                              |
|---|------------------------------|
| (1) $[\text{Ni}(\text{CO})_4]$                  | Tetracarbonylnickel(0)       |
| (2) $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ | Triamminetrinitrocobalt(III) |
| (3) $[\text{Fe}(\text{CO})_5]$                  | Pentacarbonyliron(0)         |

## SHAPES OF COMPLEX IONS WITH COORDINATION NUMBER 2, 4 AND 6

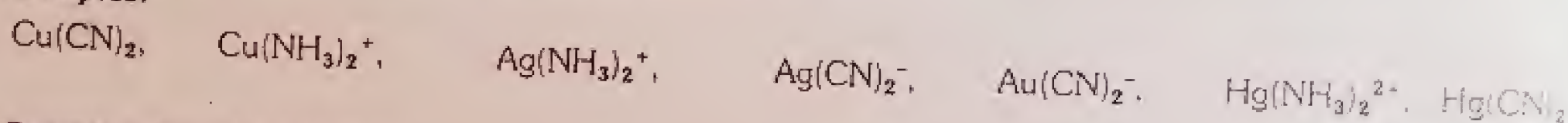
Exercise Q3(iii) (a) Explain shapes and origin of colors of coordination compounds.

- The coordination number shown by metals in complexes are 2 to 9.
- The most common are 2, 3 and 6.
- Geometries corresponding to C.N.'s = 2, 3, 4 and 5 are shown in Fig. 14.3

### (1) Coordination Number 2

The complexes having C.N.=2 are linear, since this geometry provides minimum ligand-ligand repulsion.  $\text{Cu}^+$ ,  $\text{Ag}^+$  and in some cases  $\text{Hg}^{+2}$  form such complexes.

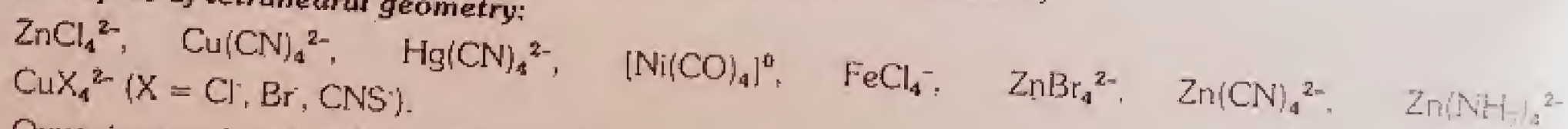
Examples:



### (2) Coordination Number 4

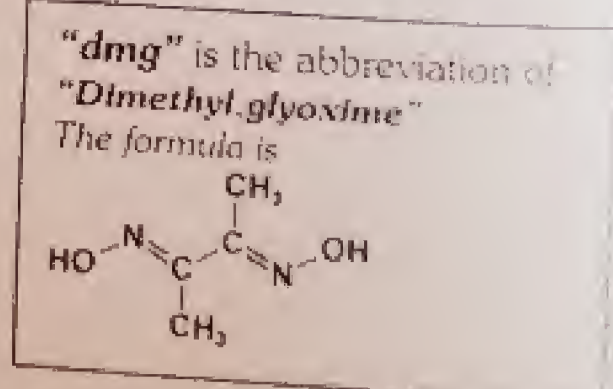
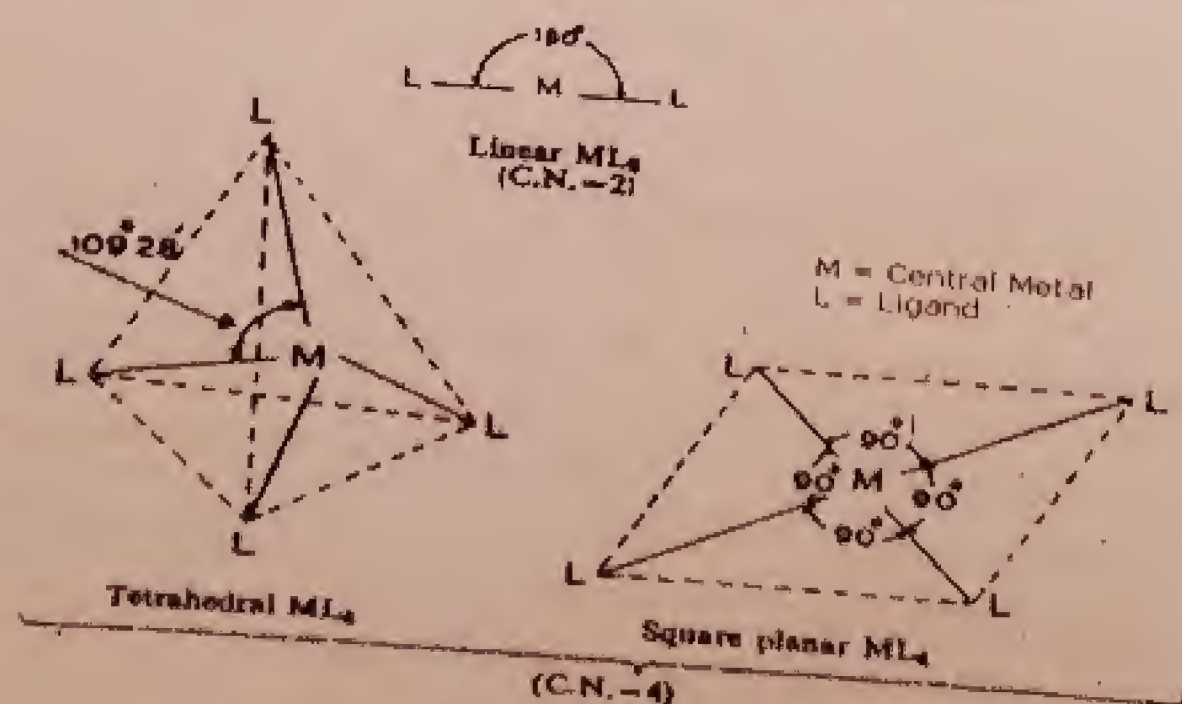
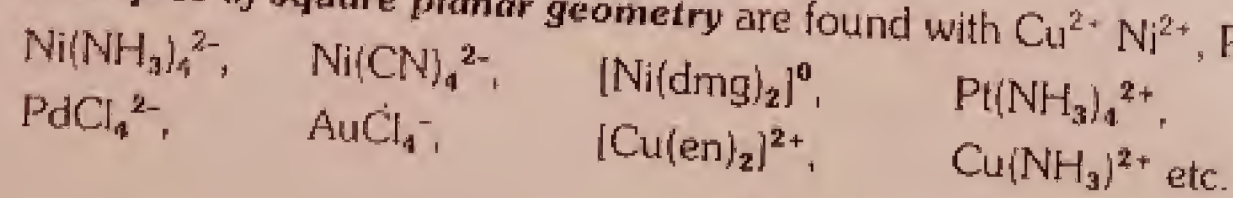
Complexes with C.N.=4 may be tetrahedral or square planar in geometry.

Examples of tetrahedral geometry:



Oxyanions such as  $\text{VO}_4^{3-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{FeO}_4^{2-}$  and  $\text{MnO}_4^-$  are also tetrahedral.

Examples of square planar geometry are found with  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pt}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Au}^{3+}$  etc. ions

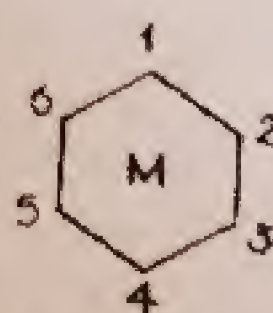




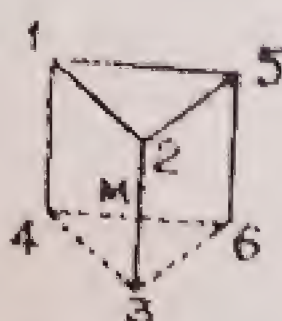
### Coordination Number 6

Complexes with  $C.N = 6$  are the most common ones formed by transition metal ions

- Six ligands in a 6-coordination compound may be arranged round the central metal ion,  $M$ , in following ways
  - ✓ at the corners of hexagonal plane or
  - ✓ at the apices of a trigonal prism or
  - ✓ at the apices of a regular octahedron.
- These arrangements are shown in the fig.
- An extensive study of the geometrical and optical isomers of complexes with  $C.N = 6$  has shown that arrangement of six ligands in a 6-coordination compound is always octahedral.
- The discussions of other possible geometries (i.e. hexagonal planar and trigonal prismatic geometries) are of historical interest only.



Hexagonal planar geometry



Trigonal prismatic geometry



Regular octahedral geometry

### COLOR OF COMPLEXES

- When white light is allowed to fall on a complex. The following things may occur:
  - The complex may absorb the whole of white light. In this case complex appears black.
  - The complex may reflect or transmit the whole light. In this case it appears white.
  - The complex may absorb some of it and may reflect or transmit the remaining light. In this case the complex has some color, i.e. it is colored.
- The absorption of light by the colored complexes takes place in the visible region of the spectrum which extends from  $4000\text{\AA}$  to  $7000\text{\AA}$  in wavelengths.
- The color of the absorbed light is different from that of the transmitted light. The relation between the colors of the absorbed and reflected light is shown in fig below.
- The color of the transmitted light is called the complementary color of that of the absorbed light. It is in fact the actual color of the complex.

Thus:

- Hydrated cupric sulphate containing  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}\text{SO}_4^{2-}$  ions is blue because it absorbs yellow light.
- Cupric ammonium sulphate containing  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ions is violet because it absorbs yellow green light.
- $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is purple because it absorbs green light.

The complex ions which absorb light in the infrared or ultraviolet regions of the spectrum are colorless

Examples:

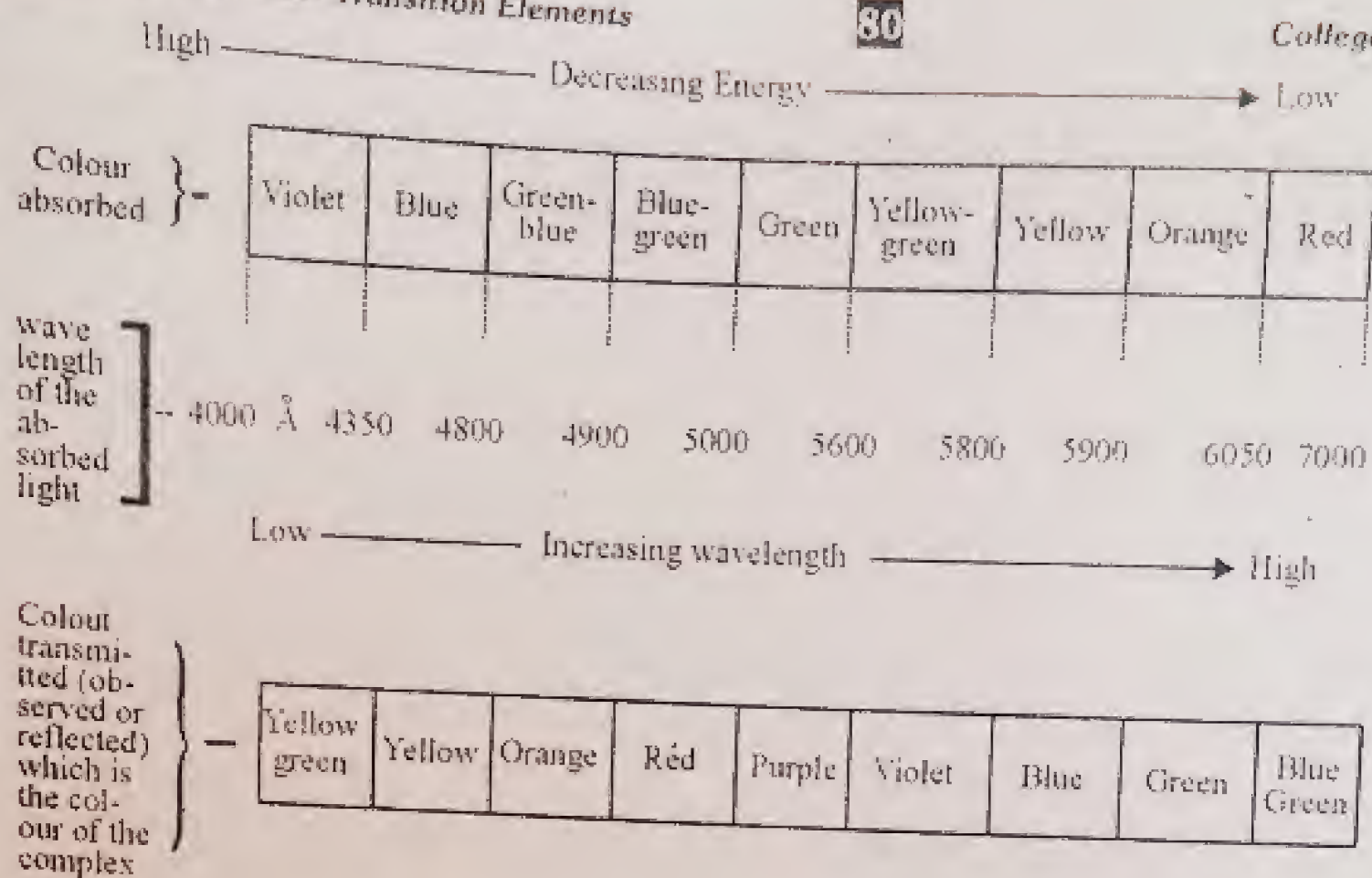
- anhydrous cupric sulphate is colorless since it absorbs light in the infrared region.
- $[\text{Cu}(\text{CN})_4]^{4-}$  ion is colorless since absorbs light in the ultraviolet region.



CH # 14: d and f-Block Elements: Transition Elements

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**Application of absorption spectrum to determine the colour of the complex**

With the help of visible absorption spectrum of a complex ion it is possible to predict the color of the complex.

**Example:**

$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  ion shows absorption maxima at a wavelength of about  $5000\text{\AA}$  which is equal to the wave number  $\bar{\nu} = 20000\text{ cm}^{-1}$ .

It can be calculated as

$$\text{Wavelength} = \lambda = 5000\text{\AA} = 5000 \times 10^{-8}\text{ cm} \quad (\text{Since } 1\text{\AA} = 10^{-10}\text{ m} = 10^{-8}\text{ cm})$$

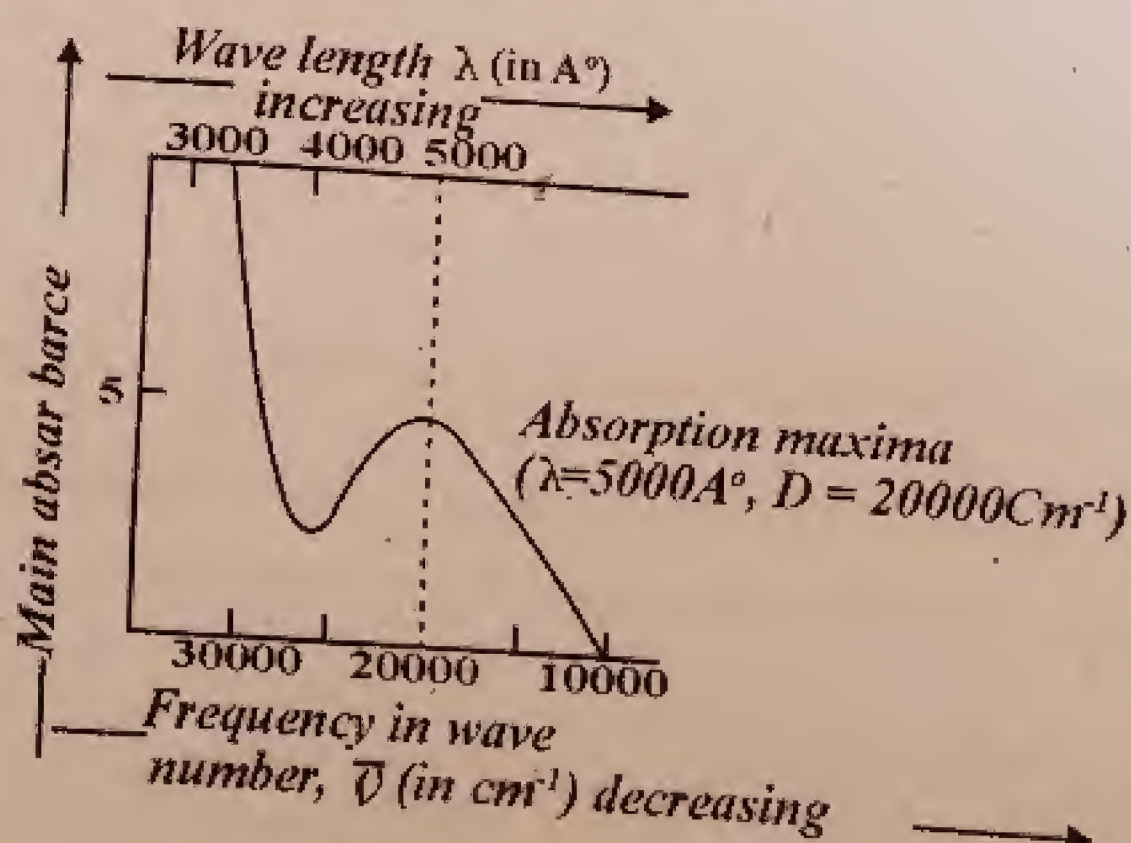
Thus

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{5000 \times 10^{-8}}$$

$$= 0.2 \times 10^5\text{ cm}^{-1} = 20000\text{ cm}^{-1}$$

Light of this wavelength ( $5000\text{\AA}$ ) is green and is absorbed by the complex ion.

Thus the transmitted light is purple, which is in fact, the color of the ions.





## QUICK QUIZ-3

1) Why do most of the transition metal ions possess a definite color?

The absorption of light by the colored complexes takes place in the visible region of the spectrum which extends from 4000Å to 7000Å in wavelengths. Since, they absorb and transmit certain radiations of visible region, most of the transition metal ions possess a definite color.

### Molecular Level Explanation

The transition metals ions have partially filled d-orbital. On complex formation, the d-orbitals are split up into two energy levels. One is of lower energy and other is of higher energy. The energy gap between the two levels corresponds to the visible region of light. Hence, when visible light falls on transition metal ion, it absorbs energy and the electron is excited from the lower energy d-orbital to the high energy d-orbital. This is called d-d transition. So, the complementary colour of absorbed light is transmitted and the complex shows colour.  
e.g.  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  is purple because it absorbs green light and transmits purple colour.

2) What is wavelength of green color

It is in the range of 5000 - 5600 Å

3) When complex compound appear black

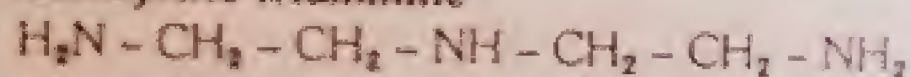
The complex may absorb the whole of white light. In this case complex appears black.

4) What will be geometry of complex compound having co-ordination number 2, 4 and 6.  
See Page 78

5) Give examples of hexadentate and tridentate ligand.

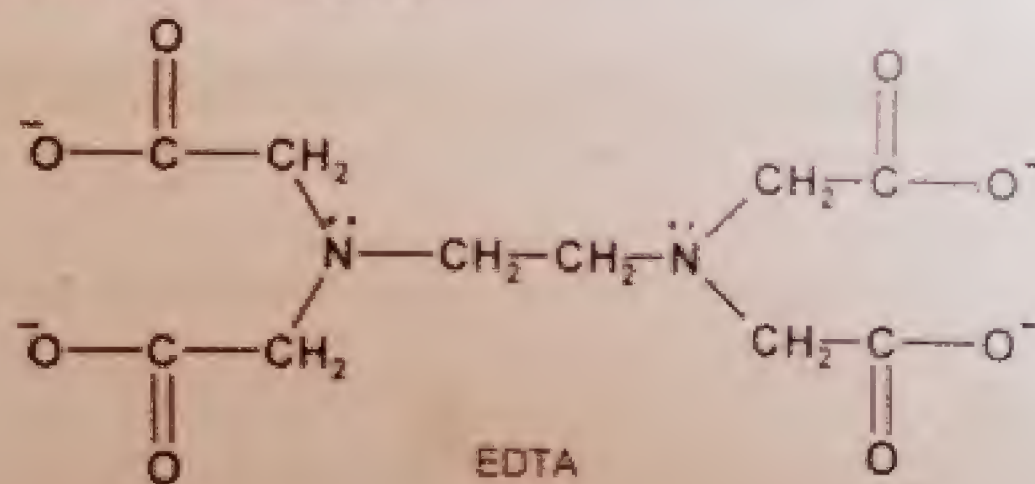
Those ligands which have three donatable electron pairs are called tridentate ligands.

Example: Diethylene triamine



Those ligands which have six donatable electron pairs are called hexadentate ligands.

Example: Ethylenediaminetetraacetate (EDTA)



## CHEMISTRY OF SOME IMPORTANT TRANSITION ELEMENTS

### VANADIUM

Vanadium is important because of

- (i) The conversion between various Vanadium Oxidation states and
- (ii) The use of Vanadium (V) oxide as a catalyst in the contact process.

### VANADIUM'S OXIDATION STATES

Vanadium has oxidation states in its compounds of +5, +4, +3 and +2. These can be inter-converted. It can be explained in terms of standard redox potentials (standard electrode potentials).




**OBSERVING THE CHANGES IN THE LAB****REDUCING VANADIUM (V) IN STAGES TO VANADIUM (II)**

The usual source of vanadium in the +5 oxidation state is ammonium metavanadate,  $\text{NH}_4\text{VO}_3$ .

- It is not very soluble in water. Therefore, it is usually first dissolved in sodium hydroxide solution.
- The solution can be reduced using zinc and an acid ( $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ ).
- The acids used are usually moderately concentrated acid.
- The exact vanadium ion present in the solution is very complicated, and varies with the pH of the solution.
- The reaction is done under acidic conditions when the main ion present is  $\text{VO}_2^+$ . It is called the dioxovanadium (V) ion.
- The reduction from +5 to +4 is shown in the figure


**Note:** The ion is usually written as  $\text{VO}_2^+$ , but is more accurately  $[\text{VO}_2(\text{H}_2\text{O})_4]^+$ .



Oxidation state = +5


$\text{VO}_2^+$

Yellow



This isn't a new oxidation state. The green is a mixture of the original yellow and the blue that is being produced.

Green



Oxidation state = +4

$\text{VO}^{2+}$


Blue

It is important to notice that the green colour produced is not actually another oxidation state. It is just a mixture of the original yellow of the +5 state and the blue of the +4.

**Do you know?**

Just like the  $\text{VO}_2^+$  ion, the  $\text{VO}^{2+}$  ion will have water molecules attached to it as well:  $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ . We usually use the simpler form.


- The reduction of V(IV) further continue and the colour changes also continue.



Oxidation state = +4

$\text{VO}^{2+}$


Blue



Oxidation state = +3

" $\text{V}(\text{H}_2\text{O})_6^{3+}$ "

Green



Oxidation state = +2

$\text{V}(\text{H}_2\text{O})_6^{2+}$

Purple

- The vanadium (III) ion is shown in inverted commas. It is because this formula is a simplification only. The exact nature of the complex ion will depend on the type of acid used in the reduction process.



### OXIDATION OF THE VANADIUM (II)

- The vanadium (II) ion is very easily oxidized to vanadium (III).
- If cotton wool is removed from the flask and some solution is poured into a test tube, it turns green because of its contact with oxygen in the air. Thus, it is oxidized back to vanadium (III).
- If it is allowed to stand for a long time, the solution finally turns blue as the air oxidizes it back to the vanadium (IV) state, i.e.,  $\text{VO}^{2+}$  ions.
- Nitric acid is a powerful oxidizing agent. If it is added to the original vanadium (II) solution, it also produces blue  $\text{VO}^{2+}$  ions. Thus vanadium (II) is again oxidized back to vanadium (IV).

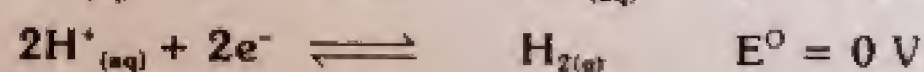
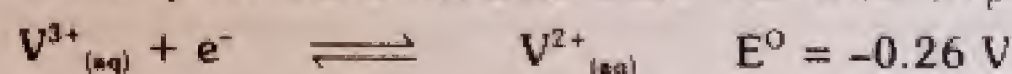
The vanadium(II) oxidation state is easily oxidized back to vanadium(III) or even higher.

### OXIDATION BY HYDROGEN IONS

- The original reduction was carried out using zinc and an acid in a flask stoppered with a piece of cotton wool to keep the air out because air will rapidly oxidize the vanadium (II) ions.
- The hydrogen ions present in the solution can also do the same.
- The vanadium (II) solution is only stable as long as you keep the air out, and in the presence of the zinc. The zinc is necessary to keep the vanadium reduced.

#### Oxidation of Vanadium (II) to Vanadium (III)

Let  $\text{H}^+$  ions are present and zinc is not there. The reduction potentials are



Since,

- The reaction with the more negative  $E^\circ$  value goes to the left (oxidation half reaction).
- The reaction with the more positive value (or less negative value) goes to the right (reduction half reaction).

Therefore,

- The vanadium (II) ions will be oxidized to vanadium (III) ions (i.e. the reaction goes to the left) and
- The hydrogen ions will be reduced to hydrogen (i.e., the reaction goes to the right).

#### Oxidation of Vanadium (III) to Vanadium (IV)

The  $E^\circ$  values are



- In order for the vanadium equilibrium to move to the left, it should have the more negative  $E^\circ$  value.
- However, it has not got the more negative  $E^\circ$  value than hydrogen. Hence, the reaction will not occur.

### OXIDATION BY NITRIC ACID

#### Oxidation of Vanadium (II) to Vanadium (III)

Consider the reduction potentials

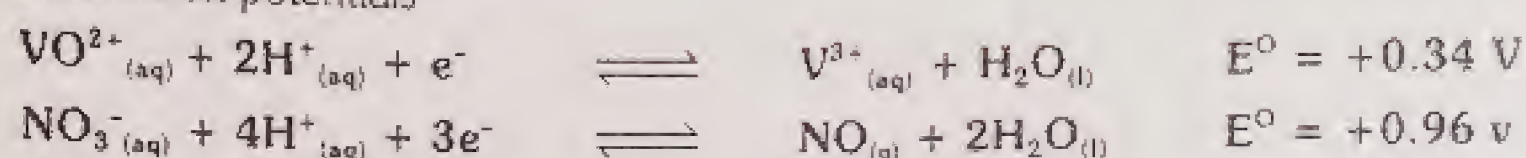


- The vanadium reaction has the more negative  $E^\circ$  value and so will move to the left.
- The nitric acid reaction moves to the right.
- Hence, nitric acid will oxidize vanadium (II) to vanadium (III).



### Oxidation of Vanadium (III) to Vanadium (IV)

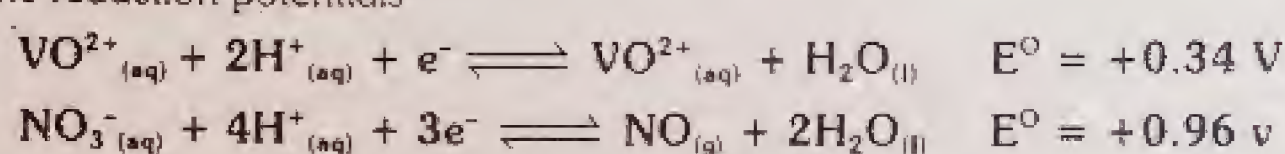
Consider the reduction potentials



- The nitric acid again has the more positive  $E^{\circ}$  value and so moves to the right.
- The more negative (less positive) vanadium reaction moves to the left.
- Hence, nitric acid will oxidize vanadium (III) to vanadium (IV).

### Oxidation of Vanadium (IV) to Vanadium (V)

Consider the reduction potentials



- If the vanadium reaction to move to the left towards dioxovanadium (V) ion, it should have the more negative (less positive)  $E^{\circ}$  value.
- However, it has not got a less positive value (or more negative value). Thus, the reaction will not occur.

*Other oxidizing agents can be analyzed in a similar way*

#### **Conclusions:**

- If  $E^{\circ}$  values show that a reaction is possible, then it should not be assumed that it will necessarily occur.
- Practically, the reaction can be too slow due to high activation energy. Therefore, it may not actually happen.

**Exercise Q3(v) (a) Discuss vanadium (V) oxide as a catalyst with example.**

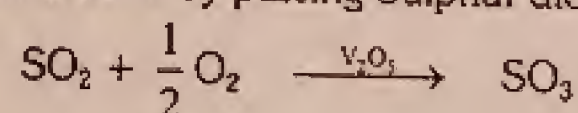
**Quick Quiz-4 (4): How  $\text{V}_2\text{O}_5$  use as catalyst for oxidation of  $\text{SO}_2$  (g)  $\rightarrow$   $\text{SO}_3$  (g)**

### **VANADIUM (V) OXIDE AS A CATALYST IN THE CONTACT PROCESS**

#### **The overall reaction**

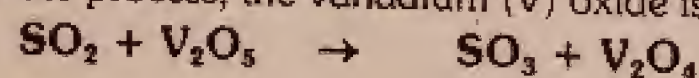
During the Contact Process for manufacturing sulphuric acid, sulphur dioxide has to be converted into Sulphur trioxide.

This is done by passing Sulphur dioxide and oxygen over a solid vanadium (V) oxide catalyst.

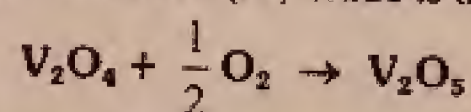


#### **How the reaction works**

- The transition metals and their compounds have ability to act as catalysts because of their ability to change their oxidation state (oxidation number).
- The Sulphur dioxide is oxidized to Sulphur trioxide by the vanadium (V) oxide.
- In the process, the vanadium (V) oxide is reduced to vanadium (IV) oxide.



- The vanadium (IV) oxide is then re-oxidized by the oxygen.



- Although the catalyst has been temporarily changed during the reaction, at the end it is chemically the same as it started.



## QUICK QUIZ-4

1. Give source of vanadium in +5 oxidation state

The usual source of vanadium in the +5 oxidation state is ammonium metavanadate,  $\text{NH}_4\text{VO}_3$ .

2. How solution of  $\text{NH}_4\text{VO}_3$  is prepared

The  $\text{NH}_4\text{VO}_3$  is not very soluble in water. Therefore, it is usually first dissolved in sodium hydroxide solution.

3. How re-oxidation of lower oxidation state of vanadium is prevented

The vanadium in lower oxidation state can be easily re-oxidized by atmospheric oxygen. It can be prevented if air is kept out of flask, and in the presence of the zinc. Zinc is a reducing agent so it keeps the vanadium reduced.

4. How  $\text{V}_2\text{O}_5$  use as catalyst for oxidation of  $\text{SO}_2$  (g)  $\rightarrow$   $\text{SO}_3$  (g)

See Page 84

## CHROMIUM

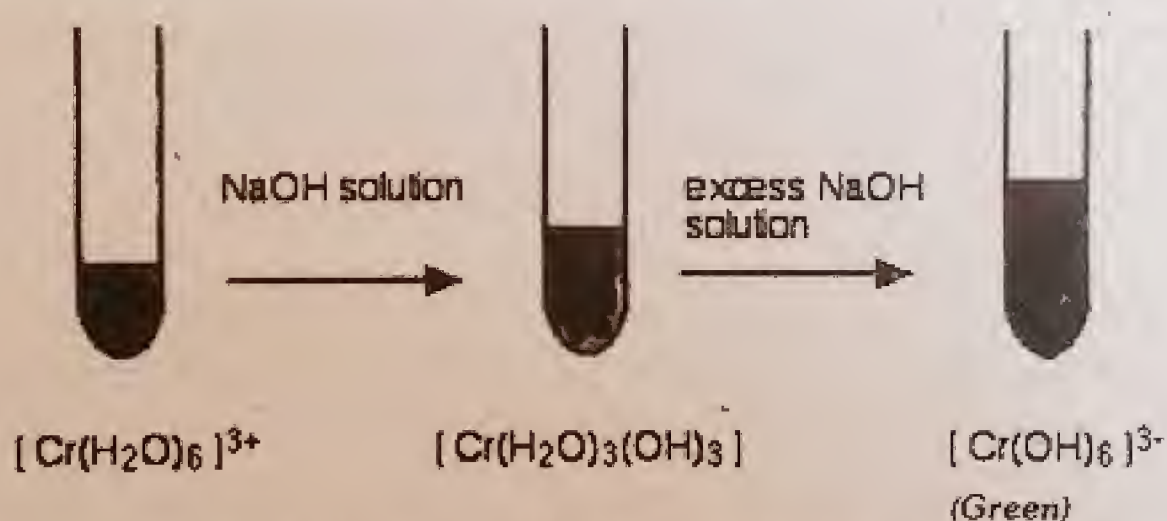
The important discussion is;

- (i) The interconversion of the various oxidation states of chromium.
- (ii) The chromate (VI)-dichromate (VI) equilibrium;
- (iii) The use of dichromate (VI) ions as an oxidizing agent (including titrations).

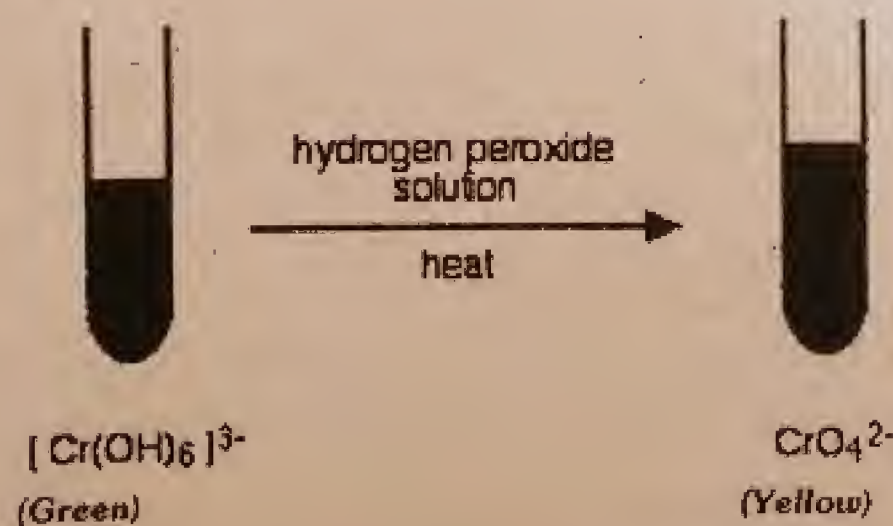
Exercise Q3(v) (b) How does chromium (III) changes to chromium (VI)?

### THE OXIDATION OF CHROMIUM(III) TO CHROMIUM(VI)

- An excess of sodium hydroxide solution is added to a solution of the hexaaquachromium(III) ions to produce a solution of green hexahydroxochromate(III) ions.



- This is then oxidized by warming it with hydrogen peroxide solution. Finally a bright yellow solution containing chromate(VI) ions is obtained.



The equation for the oxidation stage is:





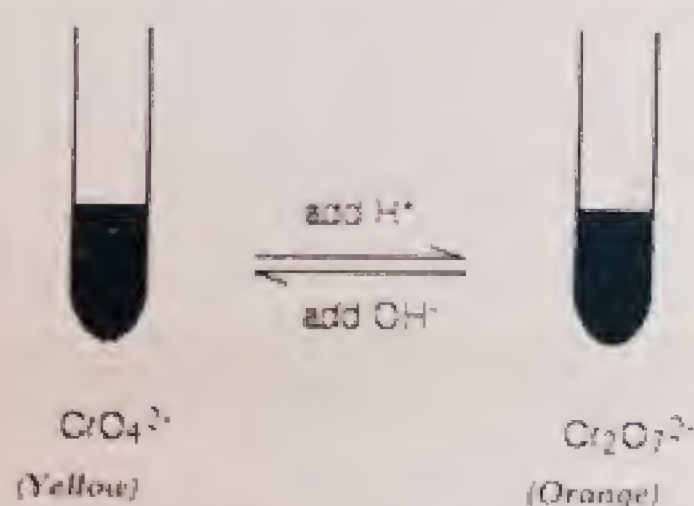
**SOME CHROMIUM(VI) CHEMISTRY****THE CHROMATE(VI)-DICHROMATE(VI) EQUILIBRIUM**

The colours of Chromium ion are:

- orange dichromate (VI) ion,  $\text{Cr}_2\text{O}_7^{2-}$ .
- yellow chromate(VI) ion,  $\text{CrO}_4^{2-}$ .

These two can be inter-converted as below:

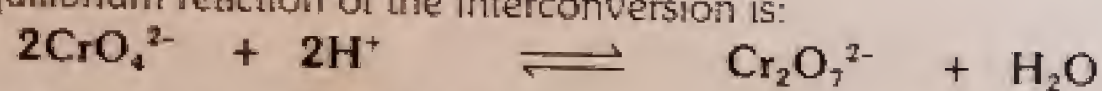
- If dilute sulphuric acid to the yellow solution it turns orange.
- If sodium hydroxide solution is added to the orange solution it turns yellow.

**The most important Precaution**

- Let the yellow chromate(VI) ions are just produced by oxidizing chromium(III) ions using hydrogen peroxide. They cannot be converted into dichromate(VI) ions without taking a precaution first.
- In the presence of acid, dichromate(VI) ions react with any hydrogen peroxide (which is left in the solution from the original reaction).
- To prevent this, the solution is heated for some time to decompose the hydrogen peroxide into water and oxygen before adding the acid.

**Explanation of the Chromate-Dichromate equilibrium**

- The equilibrium reaction of the interconversion is:



- If extra hydrogen ions are added to this, then according to Le-Chatlier's principle, the equilibrium shifts to the right.

Adding hydrogen ions forces the  
position of equilibrium to the right



- If hydroxide ions are added, these react with the hydrogen ions. Thus, according to Le-Chatlier's principle, the equilibrium shifts to the left to replace them.

Adding hydroxide ions removes  
these hydrogen ions



The equilibrium moves to the  
left to replace hydrogen ions.



### REDUCTION OF DICHROMATE(VI) IONS WITH ZINC AND AN ACID

Dichromate(VI) ions [e.g., in potassium dichromate(VI) solution] can be reduced to chromium(III) ions and then chromium(II) ions using zinc and either dilute sulphuric acid or hydrochloric acid.

- The hydrogen is produced from a side reaction between the zinc and acid. It must be allowed to escape.
- The oxygen in air must be kept out of the reaction since it rapidly re-oxidizes chromium(II) to chromium(III).

It can be done by putting cotton wool in the top of the flask. It will allow hydrogen to go out and stops most of the air from getting in against the flow of hydrogen.



Oxidation state = +6



Oxidation state = +3



Oxidation state = +2



- The chromium(III) ion is shown in inverted commas. It is because this formula is a simplification only. The exact nature of the complex ion will depend on the type of acid used in the reduction process.
- The equations for the two stages of the reaction are:

For the reduction from +6 to +3:



For the reduction from +3 to +2:



**Exercise Q3(v) (c) Discuss potassium dichromate (VI) and Potassium manganate (VII) as an oxidizing agent in organic chemistry. (For Potassium manganate(VII) see page 92)**

### USING POTASSIUM DICHROMATE (VI) AS AN OXIDIZING AGENT IN ORGANIC CHEMISTRY

- Potassium dichromate(VI) solution acidified with dilute sulphuric acid is commonly used as an oxidizing agent in organic chemistry.
- It is a reasonably strong oxidizing agent so that it can take the whole of the organic molecule to pieces. Potassium manganate(VII) solution also has this tendency.
- It is used to:
  - ✓ oxidize secondary alcohols to ketones,
  - ✓ oxidize primary alcohols to aldehydes,
  - ✓ oxidize primary alcohols to carboxylic acids.

**Example:**

- Ethanol (a primary alcohol), is oxidized to ethanal (an aldehyde) or ethanoic acid (a carboxylic acid) depending on the conditions as given below.

- (i) **Case-I:** If the alcohol is in excess, the aldehyde is distilled off as soon as it is formed. Thus, ethanal is the main product.





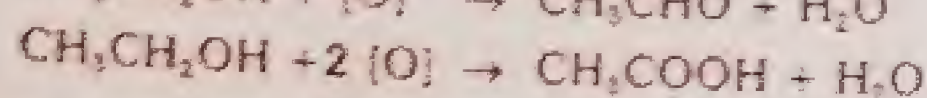
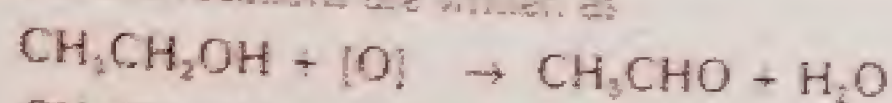


(iii) Case-II: If the oxidizing agent is in excess, the product is not allowed to escape. Thus, ethanol is further oxidized to ethanoic acid. So, ethanoic acid is the main product.

e.g. by heating the mixture under reflux (heating the flask with a condenser placed vertically in the neck), ethanoic acid is obtained.



- In organic chemistry, these equations are often simplified to concentrate only on the organic molecules.
- e.g. The above reactions are written as



The oxygen written in square brackets just means 'oxygen from an oxidizing agent'.

### USING POTASSIUM DICHROMATE(VI) AS AN OXIDIZING AGENT IN TITRATIONS

- Potassium dichromate (VI) is often used to estimate the concentration of iron(II) ions in solution.
- It serves as an alternative to using potassium manganate(VII) solution.

#### In practice

There are advantages and disadvantages in using potassium dichromate(VI).

#### Advantages

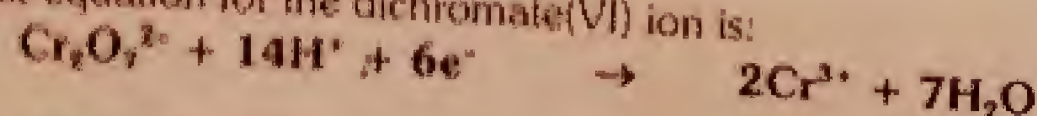
- Potassium dichromate (VI) can be used as a primary standard. It means that its stable solution of accurately known concentration can be directly prepared by weighing it. This cannot be done with potassium manganate(VII).
- Potassium dichromate (VI) can be used in the presence of chloride ions. It is possible if chloride ions are not present in very high concentration.
- Potassium manganate(VII) oxidizes chloride ions to chlorine. However, potassium dichromate(VI) is not so strong to do this. It means there are no unwanted side reactions with the potassium dichromate(VI) solution.

#### Disadvantages

- The main disadvantage lies in the colour change.
- Potassium manganate(VII) titrations are self-indicating. Potassium manganate(VII) solution is purple in colour. When it is run into the given solution, the solution becomes colourless. However, when just one drop is added in excess, the solution becomes pink. Thus, it can be detected easily. This is the end point.
- Potassium dichromate(VI) solution is orange in colour. When it is run into the given solution, the solution turns green. So, when there is one drop of orange solution in excess in a strongly coloured green solution, the colour change cannot be detected. Hence, with these titrations separate indicators are used, known as a redox indicator. Therefore, with potassium dichromate(VI) solution separate indicators are used, known as a redox indicator. These change colour in the presence of an oxidizing agent.
- There are several such indicators: such as diphenylamine sulphonate. This gives a violet-blue colour in the presence of excess potassium dichromate(VI) solution. However, the colour is made difficult by the presence of strong green colour.
- Hence, the end point of a potassium dichromate(VI) titration is not as easy to see as the end point of a potassium manganate(VII) titrations.

#### The Calculation

The half-equation for the dichromate(VI) ion is:



and for the iron(II) ions is:





Combining these two half-reaction gives the overall reaction



Thus, the reacting proportion is:

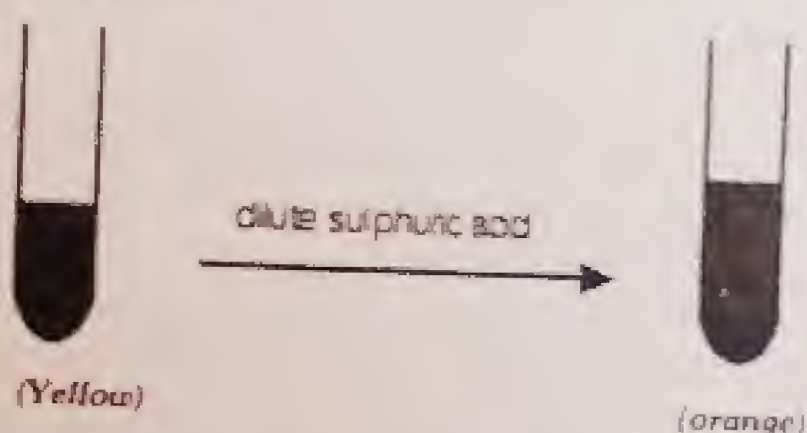
1 mole of dichromate(VI) ions : 6 moles of iron(II) ions. This mole ratio can be used for titration calculations.

### TESTING FOR CHROMATE(VI) IONS IN SOLUTION

- Typically, testing is done for solutions containing sodium, potassium or ammonium chromate (VI).
- Most chromates are only slightly soluble. Many of them are insoluble.
- The bright yellow colour of a solution suggests that it should be tested for chromate(VI) ions.

#### Testing by adding an acid

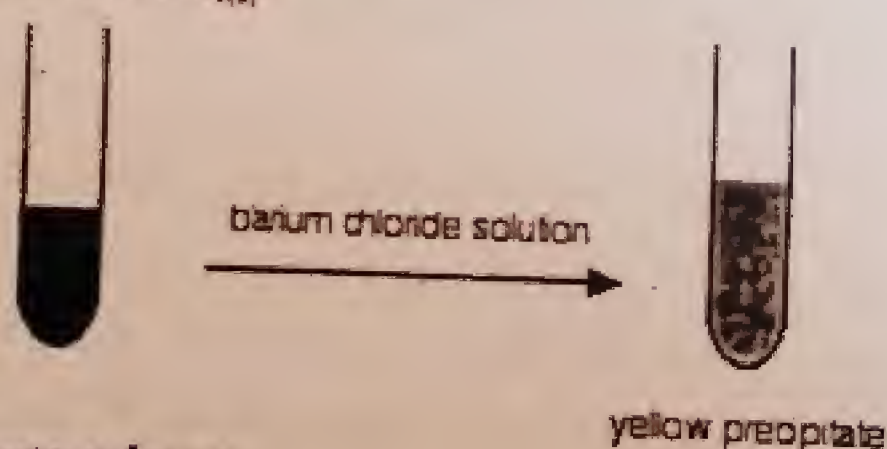
- If some dilute sulphuric acid is added to a solution containing chromate(VI) ions, the colour changes to the orange colour of dichromate(VI) ions.



This test cannot be sure for chromate(VI) ions. This colour change could be due to an acid base indicator in a solution.

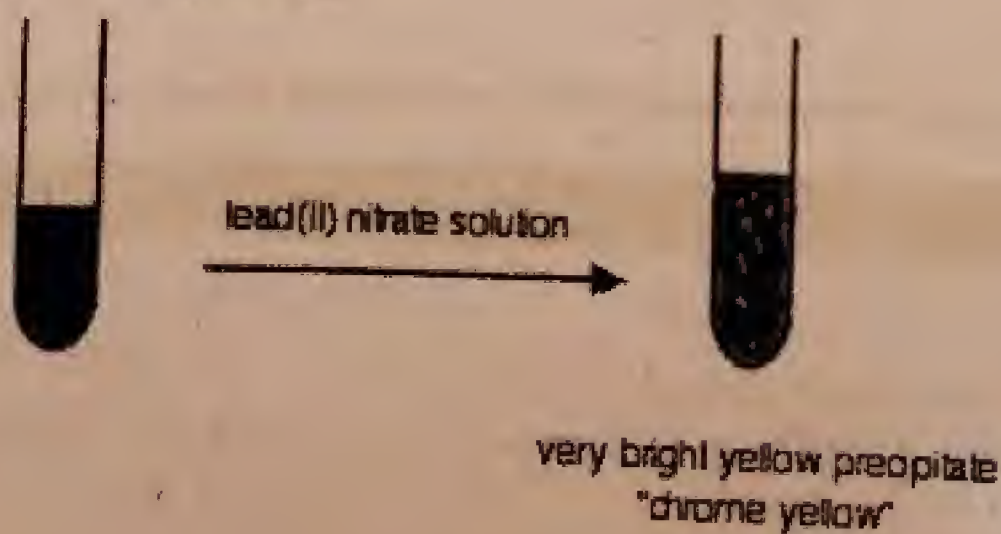
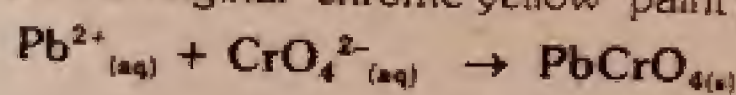
#### Testing by adding barium chloride (or nitrate) solution

Chromate(VI) ions will give a yellow precipitate of barium chromate(VI).



#### Testing by adding lead(II) nitrate solution

Chromate(VI) ions will give a bright yellow precipitate of lead(II) chromate(VI).  
PbCrO<sub>4</sub> is the original "chrome yellow" paint pigment.

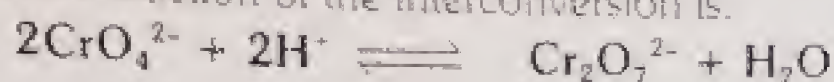




**QUICK QUIZ-5:**

(1) How dichromate ion is converted into chromate and vice versa

The equilibrium reaction of the interconversion is.

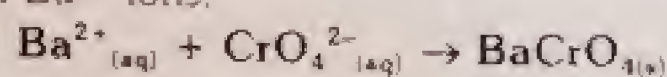


Thus

- If dilute sulphuric acid is added to the yellow solution of  $\text{CrO}_4^{2-}$  ions, it is converted into orange solution of  $\text{Cr}_2\text{O}_7^{2-}$  ions. It is because, the acid provide  $\text{H}^+$  ions, which shift the equilibrium to the right.
- If NaOH solution is added to the orange solution of  $\text{Cr}_2\text{O}_7^{2-}$  ions, it is converted into yellow solution of  $\text{CrO}_4^{2-}$  ions. It is because, the NaOH provides  $\text{OH}^-$  ions which reacts with  $\text{H}^+$  ions. Removal of  $\text{H}^+$  ions shift the equilibrium to the left.

(2) What happens when chromate ion reacts with barium chloride

The  $\text{CrO}_4^{2-}$  ions react with  $\text{Ba}^{+2}$  ions and give a yellow precipitate of barium chromate(VI). This reaction is used as a test for  $\text{Ba}^{+2}$  ions.



(3) Why potassium dichromate is preferred over potassium manganate in titration.

- Potassium dichromate (VI) can be used as a primary standard. It means that its stable solution of accurately known concentration can be directly prepared by weighing it.
- Potassium dichromate (VI) can be used in the presence of chloride ions. It is possible if chloride ions are not present in very high concentration. Thus, no unwanted side reactions occurs.

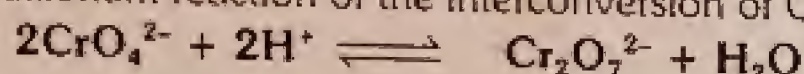
(4) In which titration end point is clear potassium dichromate or potassium manganate

- Potassium dichromate(VI) solution is orange in colour. When it is run into the given solution, the solution turns green. So, when there is one drop of orange solution is in excess in a strongly coloured green solution, the colour change cannot be detected. Hence, with these titrations separate indicators are used, known as a redox indicator.
- Potassium manganate(VII) solution is purple in colour. When it is run into the given solution, the solution becomes colourless. However, when just one drop is added in excess, the solution becomes pink. Thus, it can be detected easily. This is the end point.

(5) What color changes occur when following are added separately in potassium chromate solution

(i) Acid

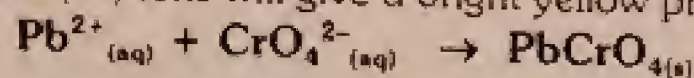
The equilibrium reaction of the interconversion of  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions is:



Thus, If dilute sulphuric acid is added to the yellow solution of  $\text{CrO}_4^{2-}$  ions, it is converted into orange solution of  $\text{Cr}_2\text{O}_7^{2-}$  ions. It is because, the acid provide  $\text{H}^+$  ions, which shift the equilibrium to the right.

(iii) Lead nitrate solution

Chromate(VI) ions will give a bright yellow precipitate of lead(II) chromate(VI).

**MANGANESE**

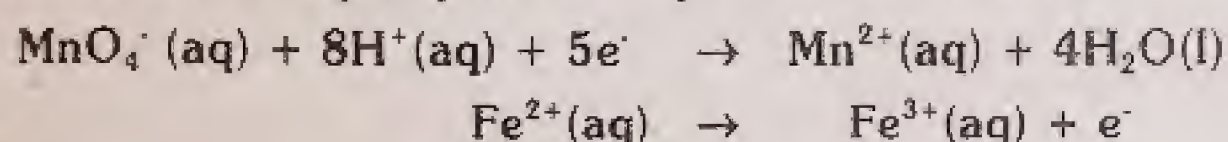
This section describes

- The Oxidation States
- Two simple reactions of manganese (II) ions in solution.
- The use of potassium manganate(VII) (potassium permanganate) as an oxidizing agent - including its use in titrations.



## THE OXIDATION STATES

- Manganese can exist in a number of oxidation states. Its most stable oxidation states are +2, +4 or +7.
- In the +7 oxidation state it exists as the intense purple ion  $\text{MnO}_4^-$ .
- It can be reduced to the pale pink  $\text{Mn}^{2+}$  by  $\text{Fe}^{2+}$  in acidic solution:



Multiply  $\text{Fe}^{2+}/\text{Fe}^{3+}$  equation by 5 and then add to the other equation to get the overall reaction.

Overall reaction:



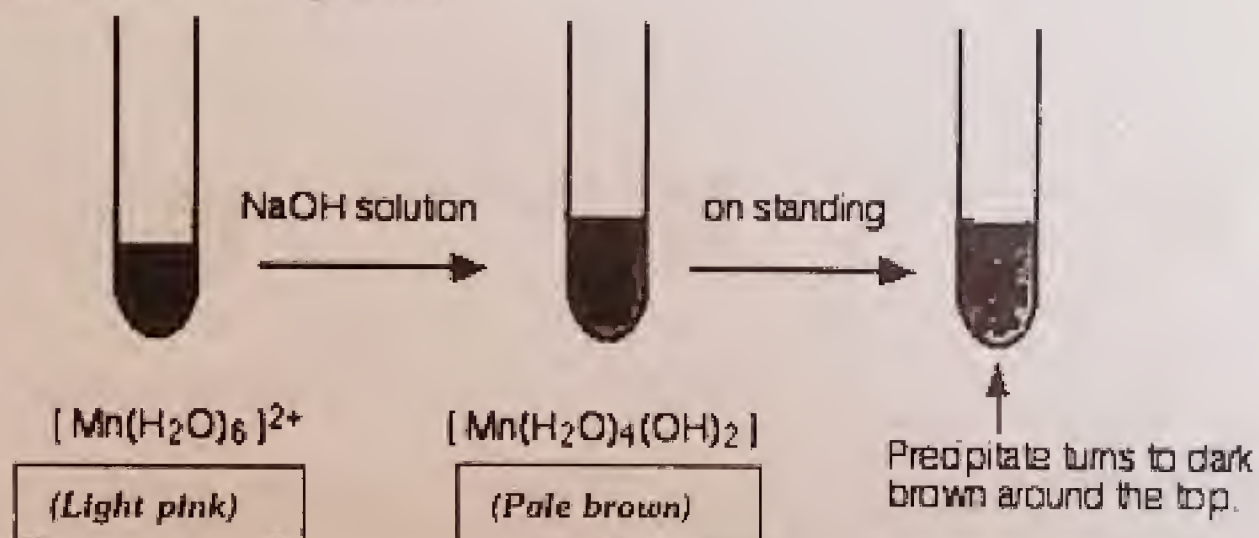
## REACTIONS OF MANGANESE (II) IONS IN SOLUTION/ OXIDATION STATES

### The reaction of hexaaquamanganese(II) ions with hydroxide ions

- Hydroxide ions (e.g. from sodium hydroxide solution) remove hydrogen ions from the water ligands attached to the manganese ion.
- Once a hydrogen ion has been removed from two of the water molecules, a complex is formed with no charge (a neutral complex). This is insoluble in water and a precipitate is formed.



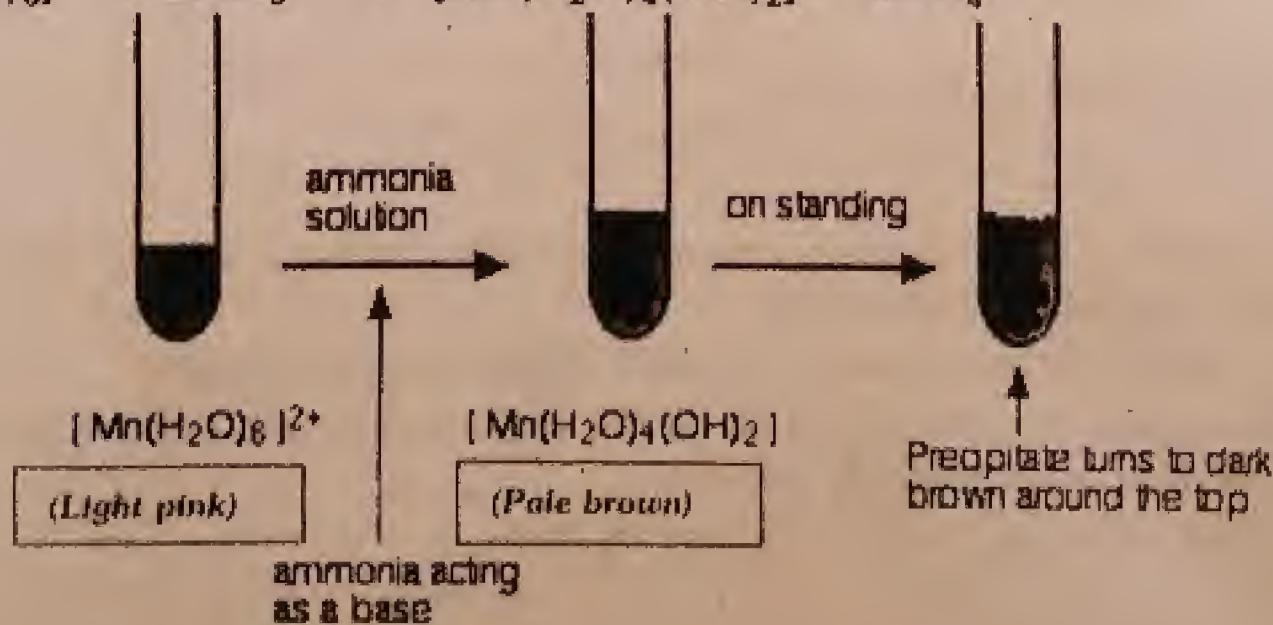
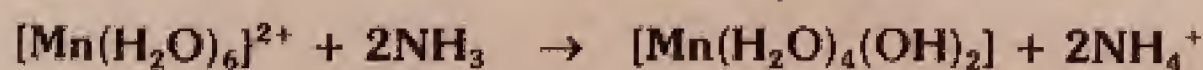
- In the test-tube, the colour changes are:



- The original solution is as very light pink as colourless.
- When this reaction occurs, the pale brown precipitate of  $[\text{Mn}(\text{H}_2\text{O})_4(\text{OH})_2]$  are formed. These are oxidized to darker brown manganese(III) oxide on contact with oxygen from the air.

### The reaction of hexaaquamanganese(II) ions with ammonia solution

- Ammonia can act as both a base and a ligand.
- In this case, it simply acts as a base at usual concentrations. Thus, it removes hydrogen ions from the aqua complex.





- 

## CH

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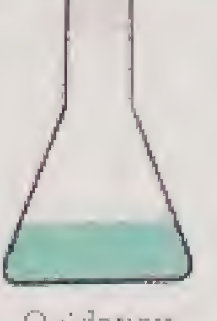

100

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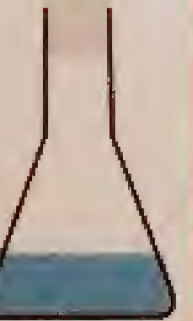


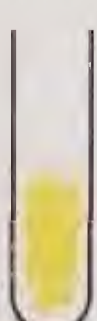







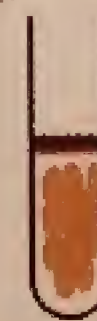



## CHEMISTRY OF VANADIUM (V): PAGE 81




					
Oxidation state = +5 $\text{VO}_2^+$	This isn't a new oxidation state. The green is a mixture of the original yellow and the blue that is being produced.	Oxidation state = +4 $\text{VO}^{2+}$	Oxidation state = +4 $\text{VO}^{2+}$	Oxidation state = +3 $\text{V}(\text{H}_2\text{O})_4^{3+}$	Oxidation state = +2 $\text{V}(\text{H}_2\text{O})_6^{2+}$

## CHEMISTRY OF CHROMIUM (Cr): PAGE 85



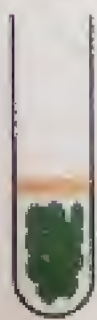
						
$\text{Cr}(\text{H}_2\text{O})_6^{3+}$	NaOH solution $[\text{Cr}(\text{H}_2\text{O})_4(\text{OH})_2]$	Excess NaOH solution $[\text{Cr}(\text{OH})_4]^-$	$[\text{Cr}(\text{OH})_4]^-$	Hydrogen peroxide solution heat $[\text{CrO}_4]^{2-}$	$\text{CrO}_4^{2-}$	Add H <sup>+</sup> Add OH <sup>-</sup> $\text{Cr}_2\text{O}_7^{2-}$
						
Oxidation state = +6 $\text{Cr}_2\text{O}_7^{2-}$	Oxidation state = +3 $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	Oxidation state = +2 $\text{Cr}(\text{H}_2\text{O})_6^{2+}$	dilute sulphuric acid add $\text{CrO}_4^{2-}$ → $\text{Cr}_2\text{O}_7^{2-}$	Barium chloride solution Yellow precipitate $\text{Ba}^{2+} + \text{CrO}_4^{2-} \rightarrow \text{BaCrO}_4$	Lead (II) nitrate solution Very bright yellow precipitate "chrome yellow" $\text{Pb}^{2+} + \text{CrO}_4^{2-} \rightarrow \text{PbCrO}_4$	

## CHEMISTRY OF MANGANESE (Mn): PAGE 90

					
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	NaOH solution $[\text{Mn}(\text{H}_2\text{O})_4(\text{OH})_2]$	on standing Precipitate turns to dark brown around the top	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	Ammonia solution ammonia acting as a base $[\text{Mn}(\text{H}_2\text{O})_4(\text{OH})_2]$	on standing Precipitate turns to dark brown around the top

		
Original dark purple manganate (VII) ion $\text{MnO}_4^-$	Reduced to dark green manganate (VI) ion $\text{MnO}_4^{2-}$	Further reduced to black precipitate of $\text{MnO}_2$

## CHEMISTRY OF IRON (Fe): PAGE 95

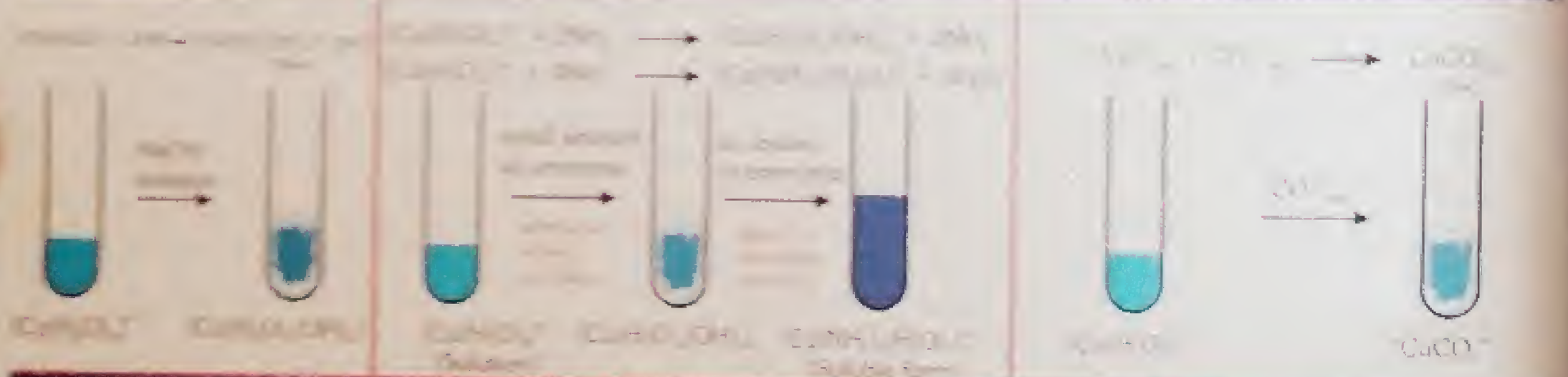
		
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	NaOH solution $[\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2]$	on standing Precipitate darkens and turns orange around the top



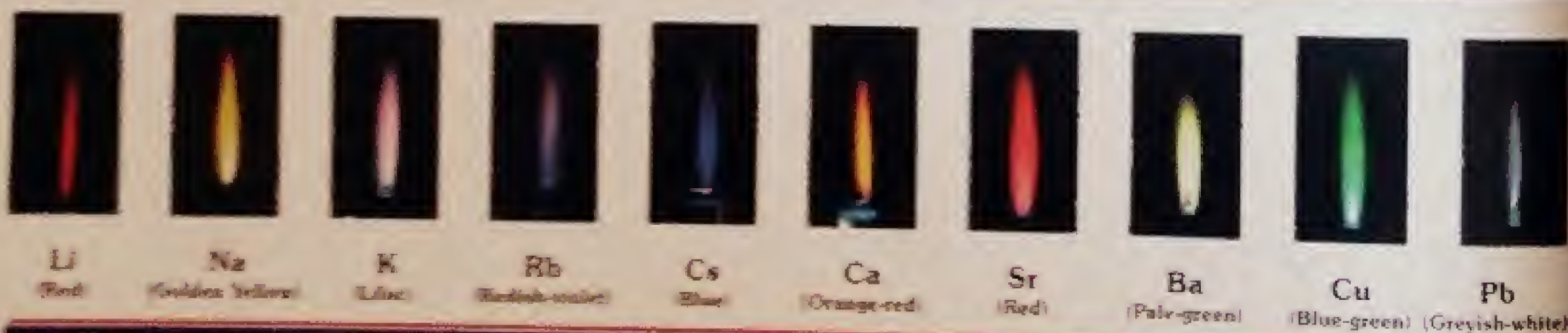
### CHEMISTRY OF IRON (Fe) PAGE 95



### CHEMISTRY OF COPPER (Cu) PAGE 99



### FLAME COLOURS (PAGE 27)



### LASSAIGNE'S TEST (PAGE 120)



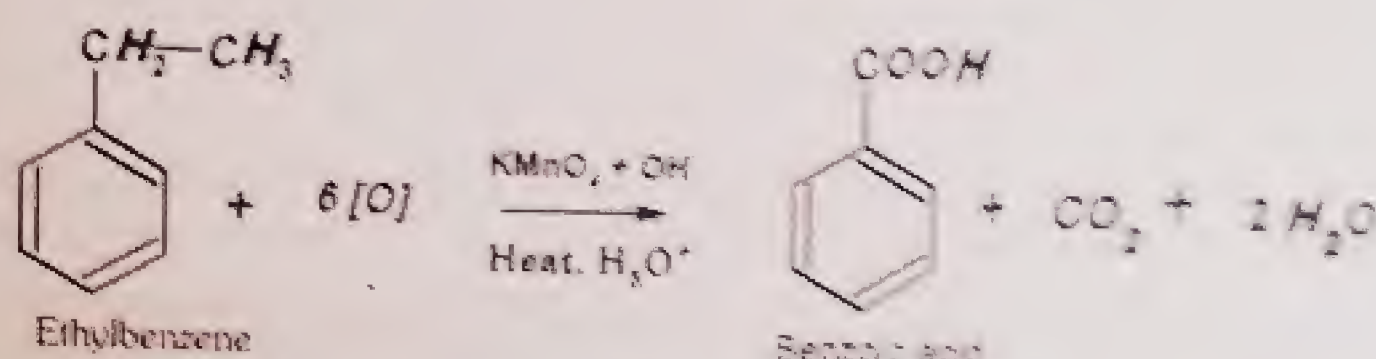
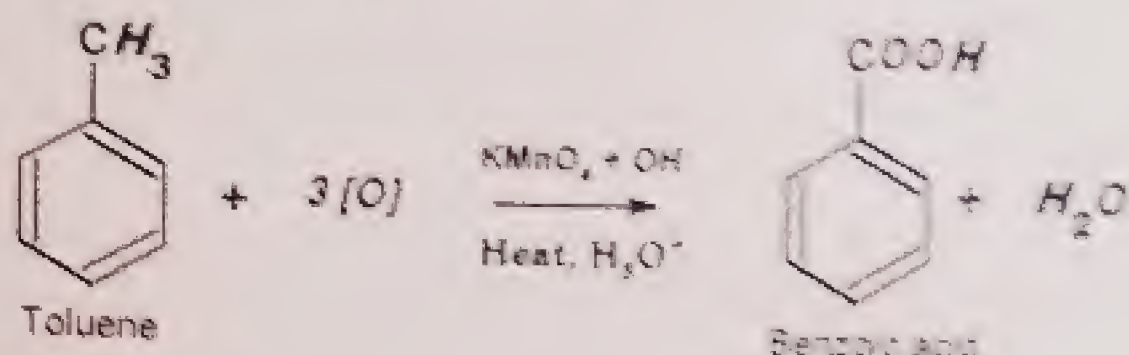
Test for Halogens  
(White = Cl<sup>-</sup>, Pale yellow = Br<sup>-</sup>, Yellow = I<sup>-</sup>)



### (iii) In the oxidation of aromatic side chains

- Alkaline potassium manganate(VII) solution oxidizes any hydrocarbon side chain attached to a benzene ring to -COOH group. Prolonged heating is necessary.

#### Examples



- In the case of the ethyl side chain, you will also get carbon dioxide.
- With longer side chains, you will get all sorts of mixtures of other products.
- However, in each case, the main product will be benzoic acid.

### USING POTASSIUM MANGANATE(VII) AS AN OXIDIZING AGENT IN TITRATIONS

#### Background

- Potassium manganate(VII) solution is used to find the concentration of all sorts of reducing agents.
- It is always used in acidic solution.

#### Examples: It oxidizes

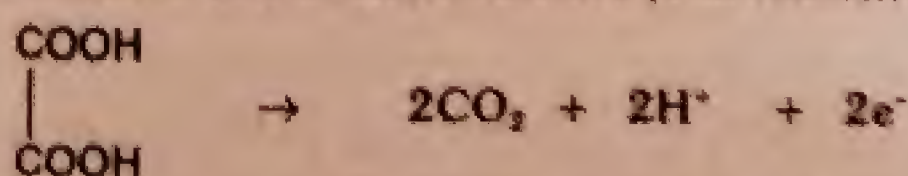
- iron(II) ions to iron(III) ions



- hydrogen peroxide solution to oxygen



- Ethanedioic acid to carbon dioxide (This reaction has to be done hot.)



- Sulphite ions (sulphate(IV) ions) to sulphate ions (sulphate(VI) ions)



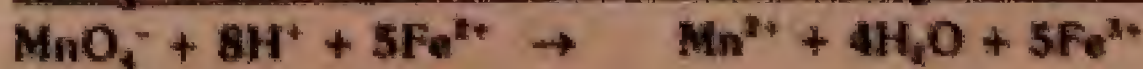
- In each case, the half-equation for the manganate(VII) ions in acidic solution is:



- These equations can be combined to give you an overall ionic equation for each possible reaction.

- From the overall reaction the reacting proportions (mole ratio) is also obtained.

e.g., Add the  $\text{Fe}^{2+}$  ions oxidation reaction to the  $\text{MnO}_4^-$  ions multiplying by suitable numbers.



Thus, the reacting proportion is:

1 mole of permanganate(VII) ions : 5 moles of iron(II) ions. This mole ratio can be used for titration calculations.



### Doing the titration

- The potassium manganate(VII) solution always taken in the burette.
- The other solution is taken in the flask and acidified with dilute sulphuric acid.
- As the potassium manganate(VII) solution is run into the flask it becomes colourless.
- Whenever there is a tiny excess of manganate(VII) ions is present in a solution a permanent light pink colour appears. This is the end point.

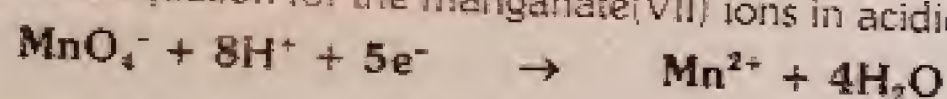
### Problems with the use of potassium manganate(VII) solution

- Potassium manganate(VII) cannot be used in titrations in the presence of ions like chloride or bromide. It is because it oxidizes them. Thus, an unknown amount of the potassium manganate(VII) would be used in side reactions. Hence, the titration result will be inaccurate. This is why the solution is not acidified with hydrochloric acid.
- Potassium manganate(VII) is not a primary standard. It means that its stable solution of accurately known concentration cannot be directly prepared by weighing it.
- Actually, it is so strongly coloured that complete dissolving of all weighed crystals cannot be detected. Moreover, it also oxidizes the water into oxygen over a period of time.
- Bottles of potassium manganate(VII) solution usually have a brown precipitate around the top. This is manganese(IV) oxide. It is produced when the manganate(VII) ions react with the water.
- So, first a solution of approximate concentration is prepared and then it is standardized by doing a titration.
- This standardization is often done by titration with ethanedioic acid (oxalic acid) solution, because it is a primary standard.

### QUICK QUIZ-6:

(1) Give half equation for manganate (VII) ion in acid solution.

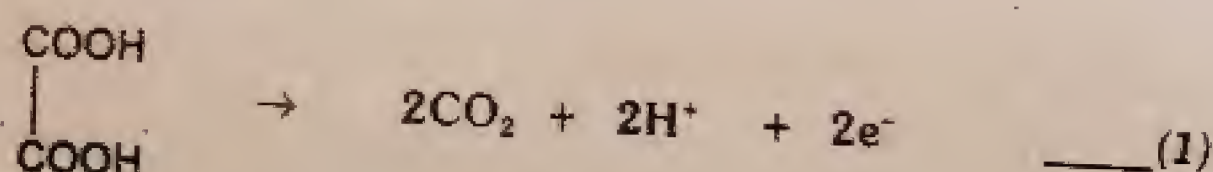
The half-equation for the manganate(VII) ions in acidic solution is:



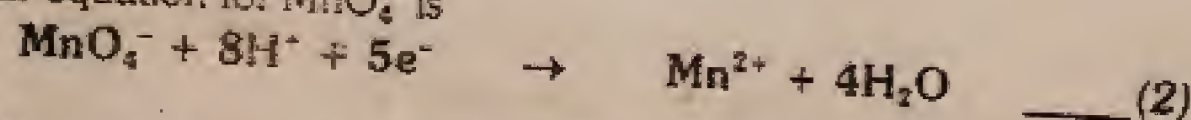
(2) Write equation for oxidation of oxalic acid

Ethanedioic acid (oxalic acid) is oxidized by  $\text{KMnO}_4$  to carbon dioxide. This reaction has to be done hot.

The half-equation for oxalic acid is



The half-equation for  $\text{MnO}_4^-$  is

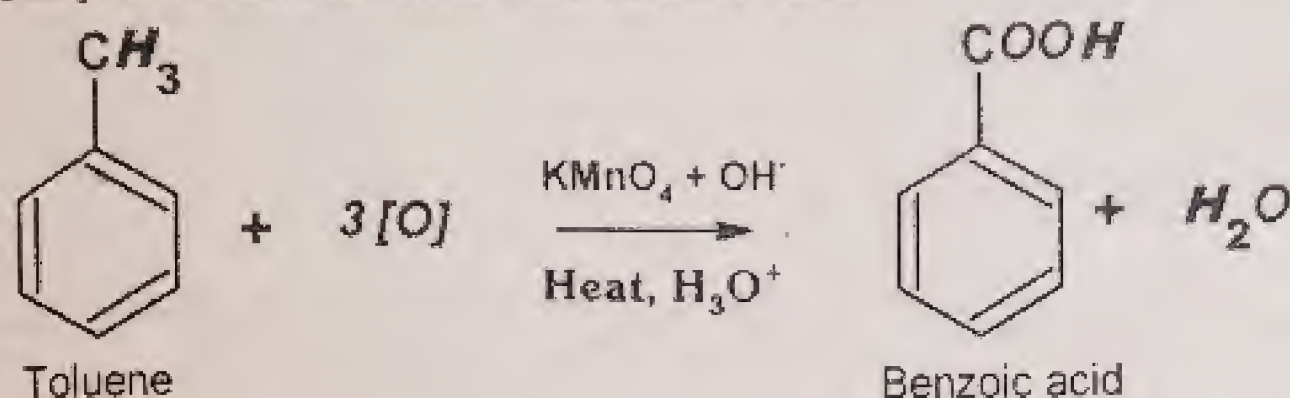


Multiplying equation (1) by 5, equation (2) by 2 and then adding them gives the overall reaction.



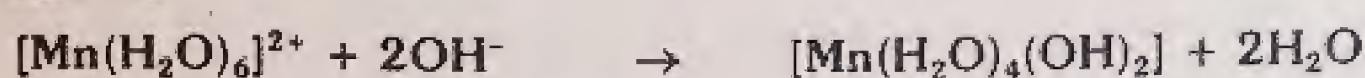


3) How can you convert toluene into benzoic acid



4) Write equation of reaction of hexaaquamanganate(II) with  $\text{OH}^-$  ion. What color change is observed

The equation is



- The original solution is as very light pink as colourless.
- When this reaction occurs, the pale brown precipitate of  $[\text{Mn}(\text{H}_2\text{O})_4(\text{OH})_2]$  are formed. These are oxidized to darker brown manganese(III) oxide on contact with oxygen from the air.

## IRON

The important points are:

- Oxidation state
- Iron as catalyst in Haber's Process and in reaction between per sulphate and iodide ions.
- Reaction of Hex aqua Iron (II) and (III) with water, ammonia, Carbonate and Thiocyanate ions.

### OXIDATION STATE

- Iron exists in two common oxidation states, +2 ( $\text{Fe}^{2+}$ ) and +3 ( $\text{Fe}^{3+}$ ).
  - In aqueous solution, the Fe is readily oxidized from  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$
- $$\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^-$$
- The  $\text{Fe}^{2+}$  ion is thus a reducing agent.
  - Thus, concentrations of  $\text{Fe}^{2+}$  in solution can be determined by titration with oxidizing agents.

### IRON AS CATALYST IN THE HABER PROCESS

- The Haber process combines nitrogen and hydrogen into ammonia.
- The nitrogen comes from the air and the hydrogen is obtained mainly from natural gas (methane).
- Iron is used as a catalyst.



### IRON IONS AS A CATALYST IN THE REACTION BETWEEN PERSULPHATE IONS AND IODIDE IONS

- The reaction between persulphate ions (peroxodisulphate ions),  $\text{S}_2\text{O}_8^{2-}$ , and iodide ions in solution can be catalyzed using either iron(II) or iron(III) ions.
  - The overall equation for the reaction is:
- $$\text{S}_2\text{O}_8^{2-} + 2\text{I}^- \rightarrow 2\text{SO}_4^{2-} + \text{I}_2$$
- Let the catalyst is iron(II) ions.
  - The reaction occurs in two stages.
- $$\begin{array}{l}
 \text{S}_2\text{O}_8^{2-} + 2\text{Fe}^{2+} \rightarrow 2\text{SO}_4^{2-} + 2\text{Fe}^{3+} \\
 2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2
 \end{array}$$
- If iron(III) ions are used then the second of these reactions occurs first.
  - This is another example of the transition metal compounds to act as catalysts because of their ability to change oxidation state.



## REACTIONS OF IRON IONS IN SOLUTION

The simplest ions of iron in solution are:

- the hexaaquairon(II) ion:  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ .
- the hexaaquairon(III) ion:  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ .

### (I) Reactions of the Iron Ions with hydroxide ions

- Hydroxide ions (e.g. from sodium hydroxide solution) remove hydrogen ions from the water ligands attached to the iron ion.
- Once enough hydrogen ion has been removed from the water molecules, a complex is formed with no charge (a neutral complex). This is insoluble in water and a precipitate is formed.

**In the Iron(II) case:**

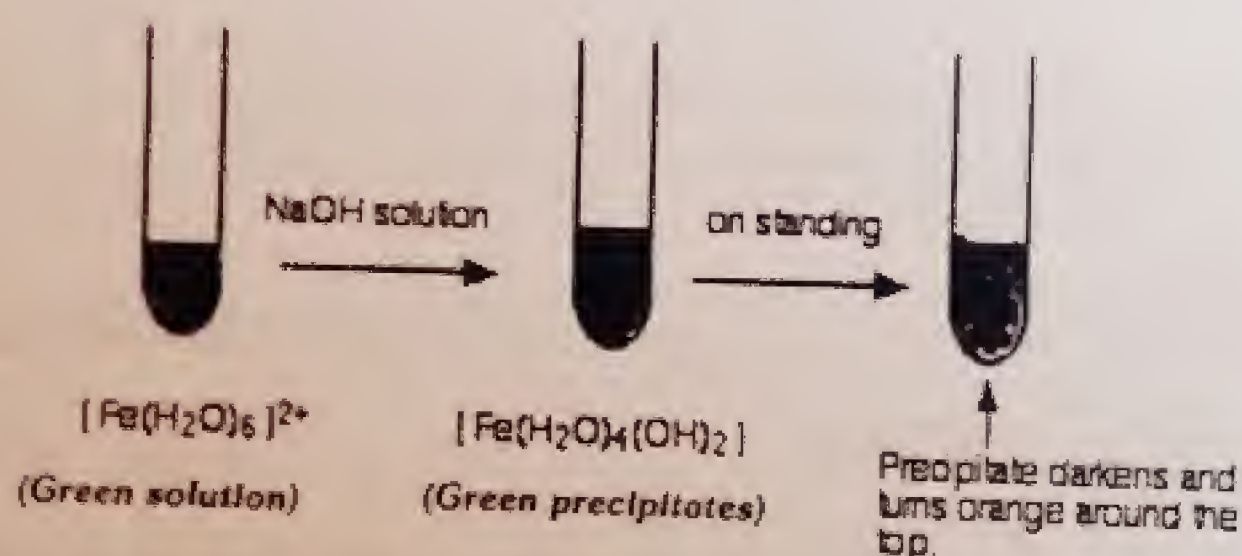


**In the Iron(III) case:**



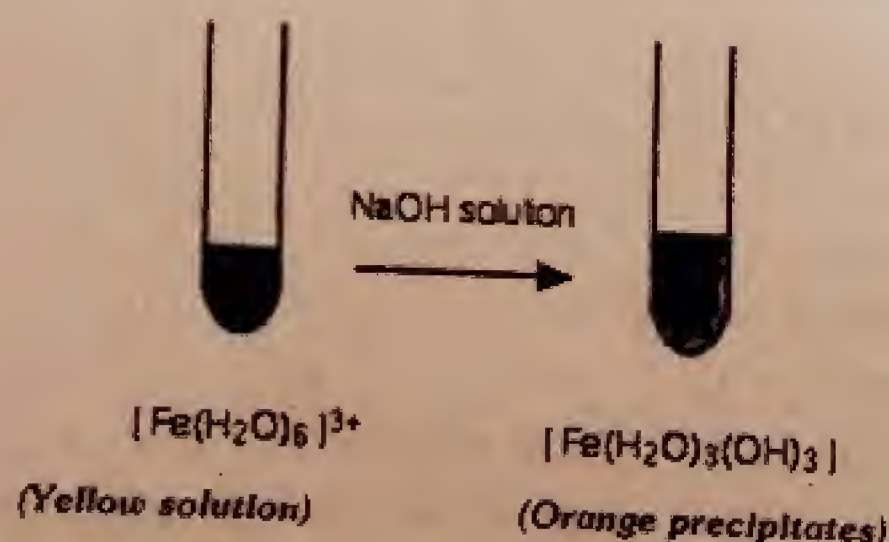
- In the test-tube, the colour changes are:

**In the Iron(II) case:**



- Iron is very easily oxidized under alkaline conditions.
- Oxygen in the air oxidizes the iron(II) hydroxide precipitate to iron(III) hydroxide especially around the top of the tube.
- The darkening of the precipitate comes from the same effect.

**In the Iron(III) case:**

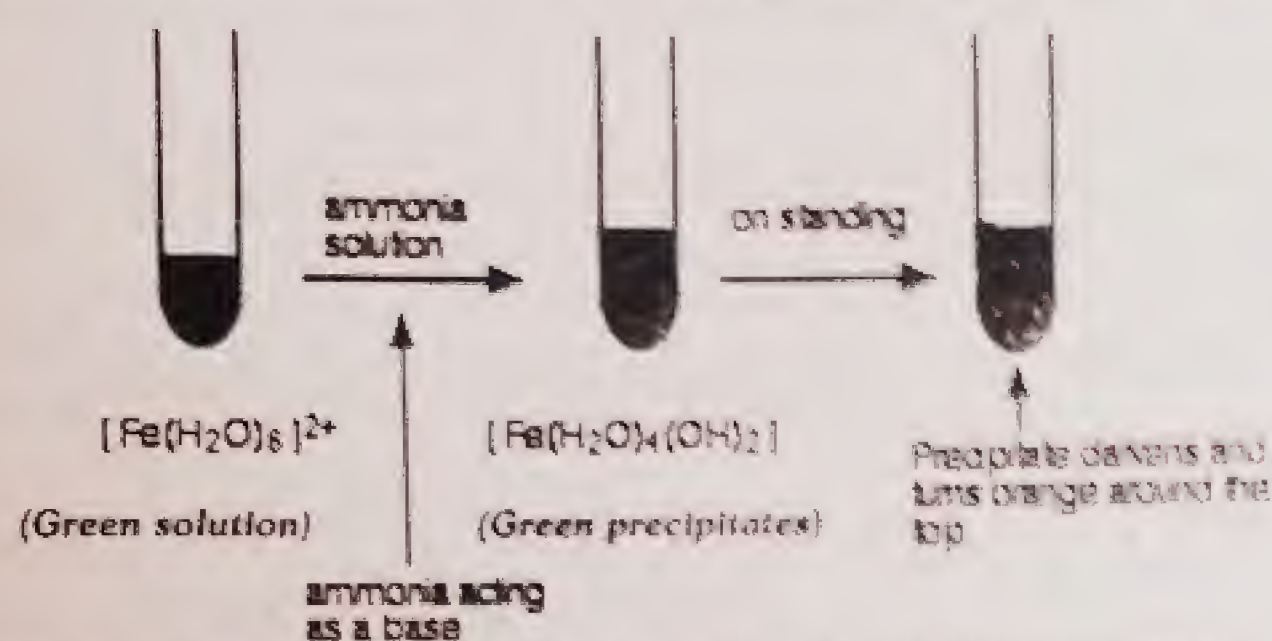




### Reactions of the iron ions with ammonia solution

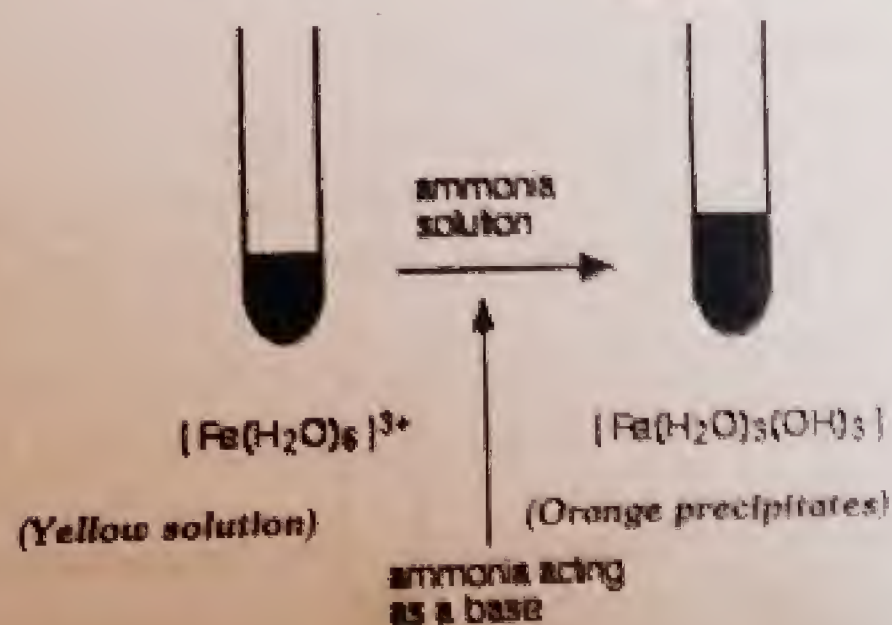
- Ammonia can act as both a base and a ligand.
- In these cases, it simply acts as a base. Thus, it removes hydrogen ions from the aqua complex.

In the Iron(II) case:



- The appearance is just the same as in when you add sodium hydroxide solution.
- The precipitate again changes colour as the iron(II) hydroxide complex is oxidized by the air to iron(III) hydroxide.

In the Iron(III) case:



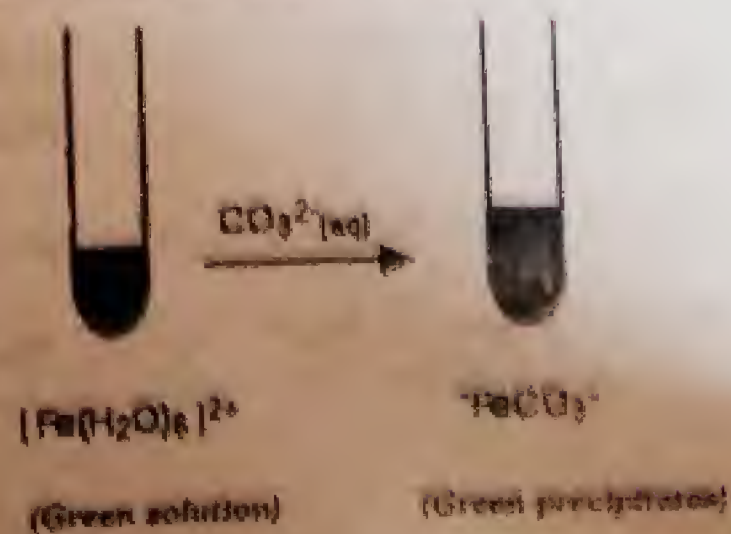
The reaction looks just the same as when you add sodium hydroxide solution.

### (iii) Reactions of the iron ions with carbonate ions

There is an important difference here between the behaviour of iron(II) and iron(III) ions.

#### (a) Iron(II) ions and Carbonate ions

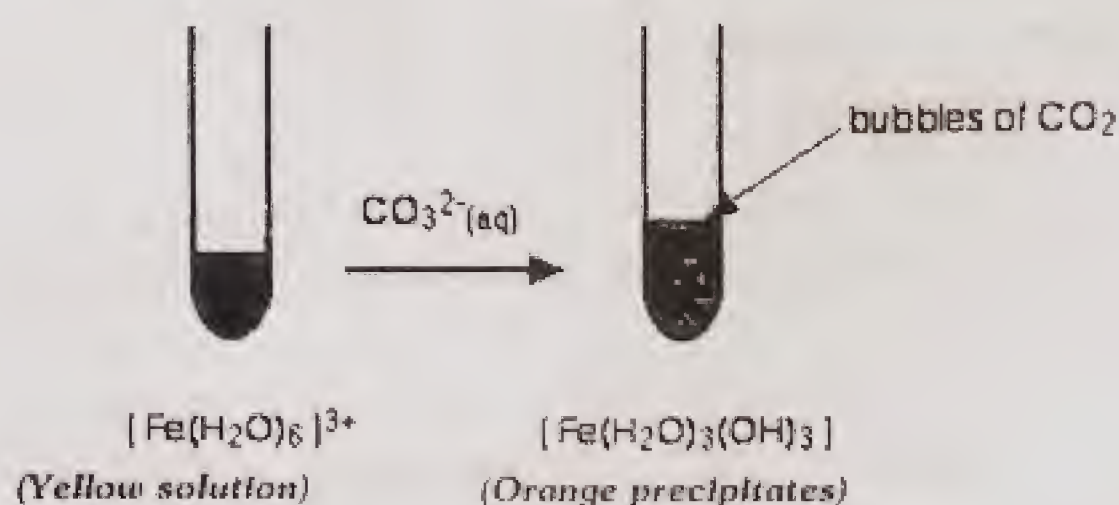
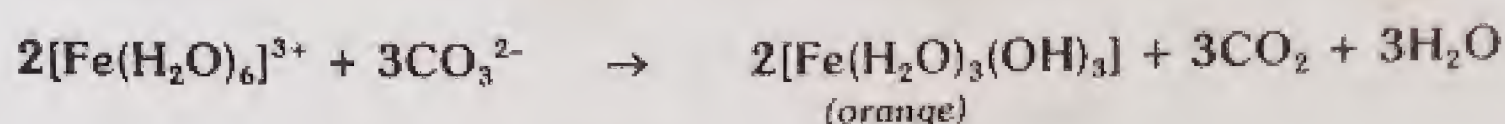
The precipitates of iron(II) carbonate are produced.





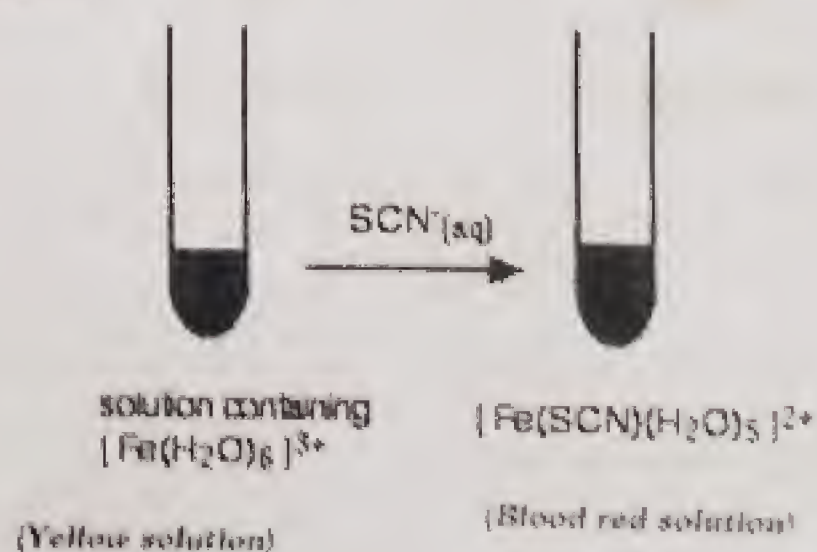
**(b) Iron(III) ions and Carbonate ions**

- The hexaaquairon(III) ion is sufficiently acidic to react with the weakly basic carbonate ion.
- If sodium carbonate solution is added to a solution of hexaaquairon(III) ions, the same precipitates are obtained as with sodium hydroxide solution or ammonia solution.
- This time, it is the carbonate ions which remove hydrogen ions from the hexaaqua ion and produce the neutral complex.
- Depending on the proportions of carbonate ions to hexaaqua ions, there are two possibilities for side products.
  - ✓ either hydrogencarbonate ions are formed
  - ✓ or carbon dioxide gas is formed from the reaction between the hydrogen ions and carbonate ions.
- The more usually quoted equation shows the formation of carbon dioxide.



**(iv) Testing for Iron(III) ions with thiocyanate ions**

- This provides an extremely sensitive test for iron(III) ions in solution.
- If thiocyanate ions,  $\text{SCN}^-$  ions (e.g. from sodium or potassium or ammonium thiocyanate solution) are added to a solution containing iron(III) ions, an intense blood red solution containing the ion  $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$  is formed.



These combine to give the ionic equation for the reaction:





## QUICK QUIZ-7:

(1) Give role of ammonia in reaction of it with iron ion solution.

Ammonia can act both as a base and a ligand. However, with iron it simply acts as a base. Thus, it removes hydrogen ions from the aqua complexes of iron.

In the iron(II) case:



In the iron(III) case:



(2) In which form iron ion are present in aqueous solution.

Iron exists in aqueous solution as aqua complexes. These are

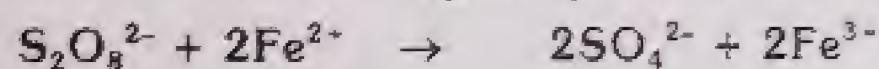
- the hexaaquairon(II) ion:  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ .
- the hexaaquairon(III) ion:  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ .

(3) Write reaction equation between persulphate ion and iodide ion.

- The overall equation for the reaction is:



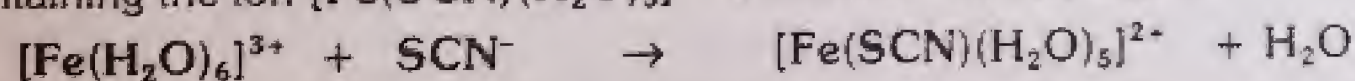
- This reaction can be catalyzed by iron ions. The reaction occurs in two stages.



- If iron(III) ions are used then the second of these reactions occurs first.

(4) How thiocyanate ion is used for testing of Fe?

If thiocyanate ions,  $\text{SCN}^-$  ions are added to a solution containing iron(III) ions, an intense blood red solution containing the ion  $[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$  is formed. The reaction is



$\text{SCN}^-$  ions are added as sodium or potassium or ammonium thiocyanate solution.

## COPPER

The important discussion includes

- The Oxidation States
- The reaction of hexaaquacopper (II) ions with hydroxide ions, Ammonia and Carbonate ion

### THE OXIDATION STATES

- Copper exists in two common oxidation states, +1 ( $\text{Cu}^+$ ) and +2 ( $\text{Cu}^{2+}$ ).
- In aqueous solution, the Cu is readily oxidized from  $\text{Cu}^+$  to  $\text{Cu}^{2+}$ :

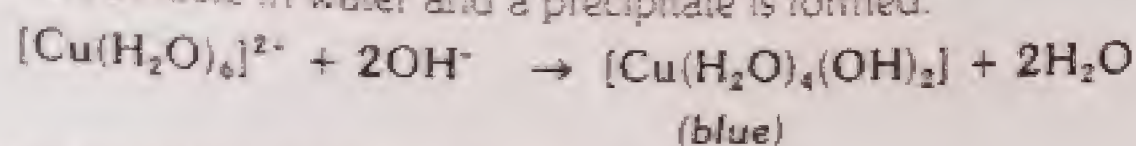


- The  $\text{Cu}^+$  ion is thus a reducing agent.
- Thus, concentrations of  $\text{Cu}^+$  in solution can be determined by titration with oxidizing agents.

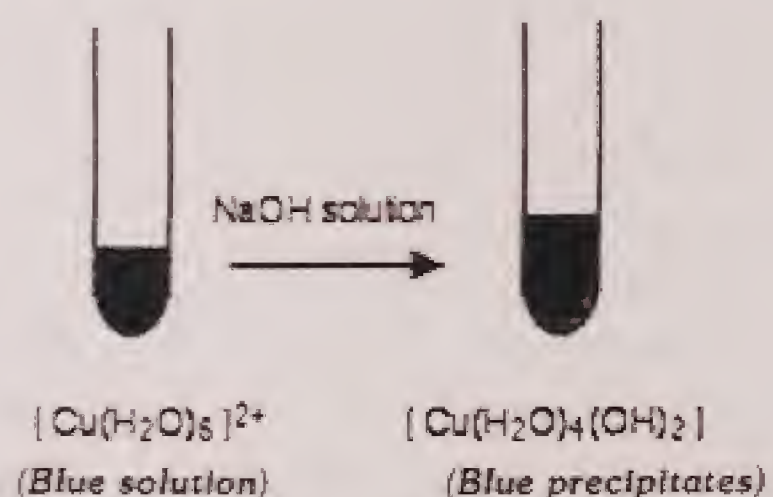


### THE REACTION OF HEXAAQUACOPPER(II) IONS WITH HYDROXIDE IONS

- Hydroxide ions (e.g. from sodium hydroxide solution) remove hydrogen ions from the water ligands attached to the manganese ion.
- Once a hydrogen ion has been removed from two of the water molecules, a complex is formed with no charge (a neutral complex). This is insoluble in water and a precipitate is formed
- This is insoluble in water and a precipitate is formed.

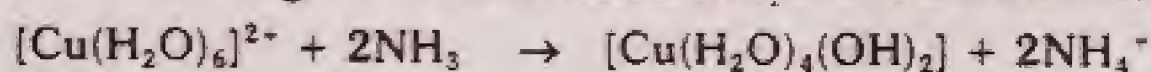


- In the test-tube, the colour change is:

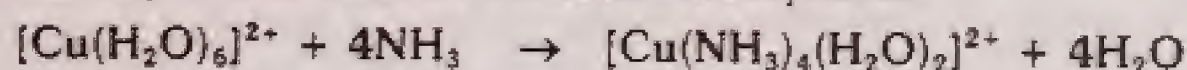


### REACTIONS OF HEXAAQUACOPPER(II) IONS WITH AMMONIA SOLUTION

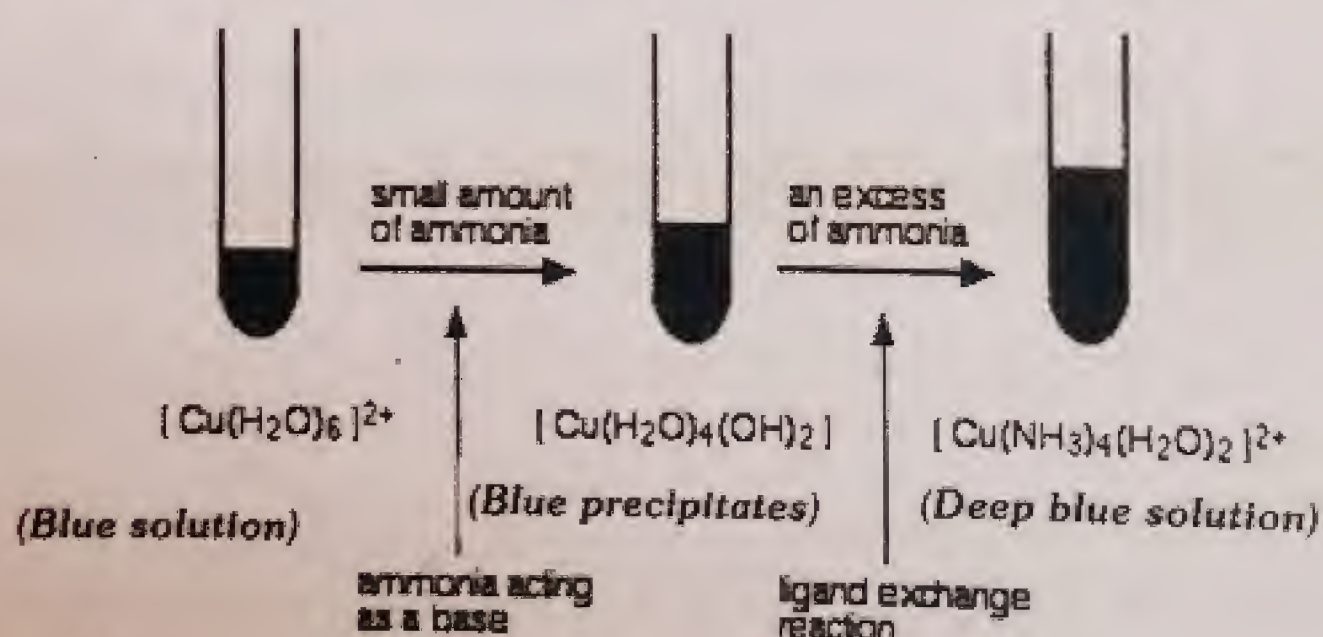
- Here, the ammonia acts both as a base and as a ligand.
- With a small amount of ammonia, hydrogen ions are pulled off the hexaaqua ion exactly as in the hydroxide ion case to give the same neutral complex. This is insoluble and precipitates are formed.



- The precipitate dissolves by adding an excess of ammonia.
- The ammonia replaces water as a ligand to give tetraamminediaquacopper(II) ions.
- Notice that only 4 of the 6 water molecules are replaced.



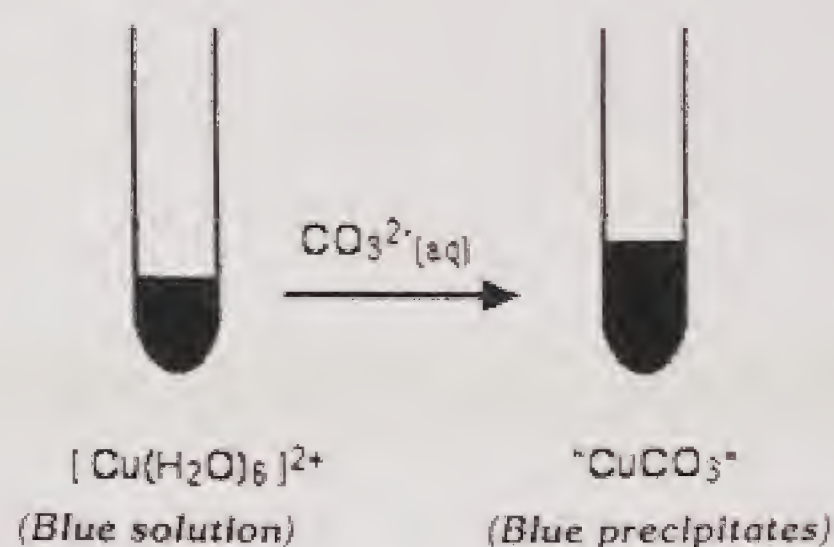
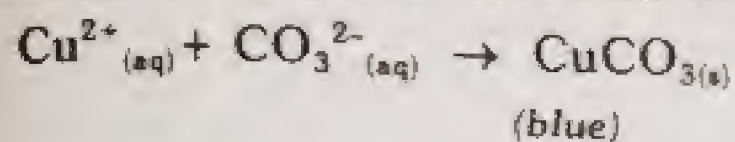
- The colour changes are:





### REACTION OF HEXAAQUACOPPER(II) IONS WITH CARBONATE IONS

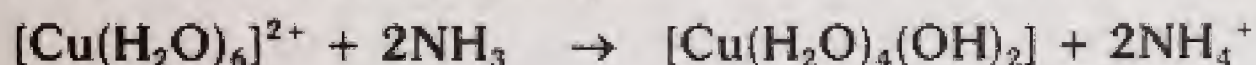
The precipitates of copper(II) carbonate are obtained.



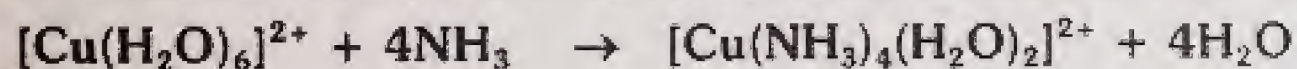
### QUICK QUIZ-8:

Ammonia acts as base as well as ligand. Prove above statement by reaction with copper ion.

- Copper ions exist as hexaaqua complex in water.
- With a small amount of ammonia, hydrogen ions are pulled off the hexaaqua ion to give the same neutral complex. This is insoluble and precipitates are formed. Here ammonia is acting as a base.



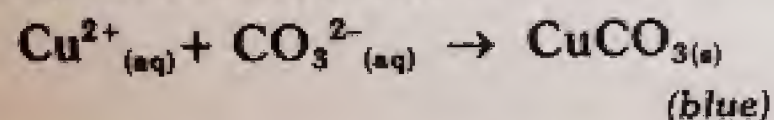
- The precipitate dissolves by adding an excess of ammonia. The ammonia replaces water as a ligand to give tetraamminediaquacopper(II) ions. Here, ammonia is acting as a ligand.



- Only 4 of the 6 water molecules are replaced.

When copper ion reacts with carbonate. What you expect. Which types of precipitate are formed?

The precipitates of copper(II) carbonate are obtained when copper (II) ions react with a carbonate.



This reaction is used as a test for copper (II) ions.

**Cu<sup>1+</sup> ion is reducing/oxidizing agent and why?**

- Copper exists in two common oxidation states, +1 (Cu<sup>1+</sup>) and +2 (Cu<sup>2+</sup>).
- In aqueous solution, the Cu is readily oxidized from Cu<sup>1+</sup> to Cu<sup>2+</sup>



- The Cu<sup>1+</sup> ion is thus a reducing agent.



## SOCIETY, TECHNOLOGY AND SCIENCE

### Transition Elements and Paints

- Certain transition elements such as Cu, Cr, etc are used in Paints.
- Mostly copper and its different compounds are used in paints.

Name of Compound	Uses
<b>Lead Monoxide</b>	(i) It is used in paints, vulcanizations of rubber and for the preparation of red lead. (ii) It is used in the manufacture of varnished, glazes, plasters and enamels. (iii) It is used in the manufacture of flint glass.
<b>Lead Suboxide</b>	(i) It is black in color and found in powder form. (ii) It is used as pigment in paints. (iii) It is used in lead storage.
<b>Lead Dioxide</b>	Lead dioxide is a reddish brown powder and used as pigment in paints.
<b>Triplumbic tetra oxide (Red Lead)</b>	(i) It is used as red paint when mixed with linseed oil. (ii) It is used in glass industry for making glazes. (iii) It is used in match industry.
<b>Basic Lead Carbonate</b>	(i) It is used as white paint for wood because of its good covering power and protection. (ii) It is used in making pottery glazes.



## EXERCISE

Select the right answer from the choices given with each question.

Coinage metals are actually

- (a) Halogens (b) Alkali metals (c) Transition metals (d) Alkaline earth metals

\_\_\_\_\_ is a transition element but it does not show variable valency because

- (a) It does not form colored salts (b) It has incomplete d-subshell  
(c) It has completely filled d-subshell (d) It has two electrons in the outermost shell

Which of the following is non-typical transition element?

- (a) Fe (b) Mn (c) Zn (d) Cr

Which elements form alloy

- (a) Alkali metals (b) alkaline earth metals (c) Halogens (d) Transition elements

Which are repelled by magnetic field?

- (a) Paramagnetic (b) Ferromagnetic (c) Diamagnetic (d) None

Magnetic moment ( $\mu$ ) of an atom or ion is the measure of its number of unpaired

- (a) Electron (b) Proton (c) Neutron (d) Nucleons

The unit of Magnetic moment is:

- (a) Coulombs (Q) (b) Amperes (A) (c) Bohr magneton (BM) (d) Watts (W)

Bronze alloy contains:

- (a) Cu and Sn (b) Ni and Cr (c) Cu and Zn (d) Cr and Fe

Give the systematic name for  $\text{Fe}(\text{CO})_5$

- (a) Pentacarbonyl iron (III) (b) Pentacarbonyl iron (I)  
(c) Pentacarbonyl iron (II) (d) Pentacarbonyl ferrate (III)

Give the chemical formula of a complex compound sodium monochloropentacyanoferrate (III).

- (a)  $[\text{Na}_5\text{FeCl}(\text{CN})_5]$  (b)  $\text{Fe}_3[\text{NaCl}(\text{CN})_5]$  (c)  $\text{Na}_5[\text{FeCl}(\text{CN})_5]$  (d)  $\text{Na}_5[\text{FeCl}(\text{CN})_5]$

The complexes having coordination number (CN) = 4 have geometry:

- (a) Tetrahedral (b) Linear (c) Square plane (d) both a and c

If we add  $\text{HNO}_3$  to the original vanadium (II) solution, it produces

- (a) blue ions (b) green ions (c) dull grey blue ions (d) pink ions

Which metal oxide is used in contact process as a catalyst:

- (a) Cr (b) Mn (c) V (d) Cu

In oxidation of chromium (III) to chromium (VI) the green color will change into

- (a) colorless (b) bright yellow (c) pink (d) None

Acidified potassium permanganate act as a strong

- (a) oxidizing agent (b) reducing agent (c) electrolytic agent (d) hydrolyzing agent

Following element shows maximum number of oxidation states?

- (a) Mn (b) Fe (c) Cr (d) Cr

The color of  $\text{Mn}^{2+}$  in hydrated form is:

- (a) Blue (b) Yellow (c) Light Pink (d) Green

Which of the following metals show more than one oxidation state?

- (a) Al (b) Mg (c) Fe (d) Ca

Iron is used as a catalyst in:

- (a) Birkland Process (b) Contact Process (c) Haber Process (d) both b and c

During the reaction of Ammonia with Iron, it acts as both a base and a:

- (a) Ligand (b) Acid (c) Iron (d) Salt

## ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (c) Transition metals

Coinage metals are actually Cu, Ag and Au. These are transition elements.

(ii) Ans: (c) Zn

It is because it has completely filled d-subshell.

The electronic configuration of  $_{30}\text{Zn}$  is  $[\text{Ar}] 4s^2 3d^{10}$ .

(iii) Ans: (c) It has completely filled d-subshell

The electronic configuration of  $_{30}\text{Zn}$  is  $[\text{Ar}] 4s^2 3d^{10}$ . Thus, it has completely filled d-subshell. So, it shows only +2 oxidation state due to loss of  $2e^-$  from 4s sub-shell.

(iv) Ans: (d) Transition elements

Transition elements have almost similar sizes and atoms of the one metal can easily take up positions in crystal lattice



**(i) Ans: (c) Diamagnetic**

By definition, the substance which is repelled by a magnetic field is called diamagnetic.

**(ii) Ans: (c) Bohr magneton (BM)**

The magnetic moment is measured by the formula  $\mu = \sqrt{n(n+2)} \text{ BM}$ , where  $n$  is the number of unpaired electrons. The magnetic moment is given in Bohr magneton (BM) units.

**(ix) Ans: (b) Pentacarbonyl iron (5)**

Since CO is a neutral ligand so in  $\text{Fe(CO)}_5$ , the oxidation state of Fe is also 0.

**(x) Ans: (d) both a and c**

e.g. In  $[\text{Ni(CO)}_4]$ , the geometry is tetrahedral and in  $[\text{Cu(NH}_3)_4]^{2+}$ , the geometry is square planar. However, both these have coordination number = 4.

**(xiii) Ans: (c) V**

Vanadium (V) is used in the form of  $\text{V}_2\text{O}_5$  as catalyst in the following reaction:



**(xiv) Ans: (a) oxidizing agent**

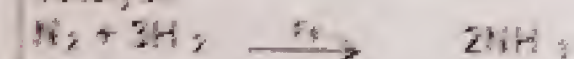
In potassium permanganate Mn atom is present in its highest oxidation state. So its oxidation state can be reduced by gaining electrons, therefore it will act as an oxidizing agent.

**(xvii) Ans: (c) Light Pink**

$\text{Mn}^{2+}$  salts are light pink in colour.

**(xi x) Ans: (c) Haber Process**

In Haber process, ammonia is produced using Fe as a catalyst.



or the other. Thus, they form substitutional alloys among themselves.

**(vi) Ans: (a) Electron**

Due to unpaired electrons, a substance shows magnetic moment and thus it is attracted towards magnetic field.

**(viii) Ans: (a) Cu and Sn**

Bronze alloy contains Cu = 90 - 95% Sn = 5 - 10%.

**(x) Ans: (c)  $\text{Na}_3[\text{FeCl(CN)}_5]$**

In  $\text{Na}_3[\text{FeCl(CN)}_5]$ , the oxidation state of Fe is III.

**(xii) Ans: (a) blue ions**

The  $\text{HNO}_3$  first oxidizes  $\text{V(II)}$  and finally to  $\text{V(V)}$  state. The salts of  $\text{V(V)}$  ions are of blue color.

**(xiv) Ans: (b) bright yellow**

Chromium in the form of  $\text{Cr(VI)}$  may exist as  $\text{CrO}_4^{2-}$  ions. It produces bright yellow solution. As  $\text{CrO}_4^{2-}$ , it produces orange solution.

**(xvi) Ans: (a) Mn**

The electronic configuration of  $\text{Mn}$  is  $[\text{Ar}] 4s^2 3d^5$ . Thus, Mn has five unpaired electrons in 3d subshell. Moreover, it has two valence electrons in 4s subshell. Thus, it shows maximum number of oxidation states which are: +1, +2, +3, +4, +5, +6, +7.

**(xviii) Ans: (c) Fe**

It is a transition element and has several unpaired electrons in d-subshell. So, it will show variable oxidation state.

**(xx) Ans: None of these**

In fact, ammonia behaves only as a base with iron(II) and iron(III) ions. It behaves both as a ligand and a base with  $\text{Cu(II)}$  ions. It takes proton from copper aqua complex. Moreover, it forms co-ordinate covalent bond with  $\text{Cu(II)}$  ions and thus form a complex with excess of ammonia.

**Q2: Give brief answers for the following questions.**

(i) Why are d-block elements called transition elements?

They are called transition elements because they show transition in properties between s and p-block elements. Thus there is a transitional between highly reactive and strongly electropositive elements of s-block which form ionic bonds and p-block elements which form covalent compounds.

(ii) Why do the d-block elements show different oxidation states?

They show variable oxidation states. It is because they have d-electrons in addition to s-electron for the purpose of bond formation. These elements have several (n-1) d and ns electrons. The energies of (n-1) d and ns orbitals are very close to each other. The (n-1) d electrons are as easily lost as ns electrons. Thus, d-block elements show different oxidation states.

(iii) Why does Mn show the maximum number of oxidation states in 3d-series?

It is because, Mn has two electrons in 4s orbital. It also has five unpaired electrons in 3d orbitals. Generally, greater the number of unpaired electrons, greater the number of oxidation states. So Mn can use 2 to 7.

lose



electrons in bond formation. Hence, Mn shows maximum number of oxidation states in 3d-series. The oxidation states of Mn are: +2, +3, +4, +5, +6 and +7.

**What is the difference between double salts and coordination or complex compounds?**

A double salt contains two salts crystallized together in one solid form.  
e.g. potash alum,  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

A complex compound contains complex ions in which ligands are attached to central metal atom/ion by coordinate covalent bonds.  
e.g.  $K_4[Fe(CN)_6]$

A double salt does not contain complex ion.

**Explain the following terms:**

(a) **Ligand**

The atom, ion (usually anions) or neutral molecule which surrounds the central metal atom or ion by donating the electron pair is called ligand.

Examples:  
In  $K_4[Fe(CN)_6]$  and  $K_3[Fe(CN)_6]$ , CN is the ligand.  
In  $[Cu(NH_3)_4]SO_4$  and  $[Ag(NH_3)_2]Cl$ ,  $NH_3$  is the ligand.

(b) **Coordination Sphere**

The central neutral atom or ion along with ligand is called coordination sphere. It is usually placed in the square brackets. It may be positively charged, negatively charged or neutral.

Examples:  
In  $K_4[Fe(CN)_6]$ , the ion  $[Fe(CN)_6]^{4-}$  is the coordination sphere of this complex compound.  
In  $[Cu(NH_3)_4]SO_4$ , the ion  $[Cu(NH_3)_4]^{+2}$  is the coordination sphere of this complex compound.

(c) **Central Metal**

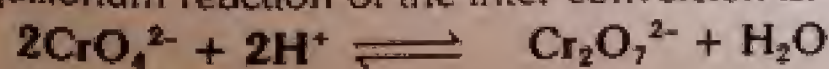
The metal atom or ion is usually a transition element. It is surrounded by a number of ligands.

Examples:  
In  $K_4[Fe(CN)_6]$ ,  $Fe^{+2}$  is the central metal ion. Six ligands (CN<sup>-</sup> ions) are surrounding it.

In  $[Cu(NH_3)_4]SO_4$ ,  $Cu^{+2}$  is the central metal ion. Four ligands ( $NH_3$  ions) are surrounding it.

**How chromate ions are converted into dichromate ions?**

The equilibrium reaction of the inter-conversion is:



If an acid is added then extra  $H^+$  ions are added to this equilibrium. Hence, according to Le-Chatelier's principle, the equilibrium shifts to the right. Thus, chromate ions are converted into dichromate ions.

Adding hydrogen ions forces the position of equilibrium to the right

Hydrogen ion





(vii) What is the difference between paramagnetism and diamagnetism?

- The substances attracted into the magnetic field are called paramagnetic and the phenomenon is called paramagnetism. It is due to the unpaired electrons present in the substances. e.g.  $Mn^{+2}$  ions *Odd*
- The substances which are slightly repelled by magnetic field are called diamagnetic and the phenomenon is called diamagnetism. It is found in substances in which even number of electrons are present, and thus have paired spins. e.g.  $Zn^{+2}$  ions *Pair*

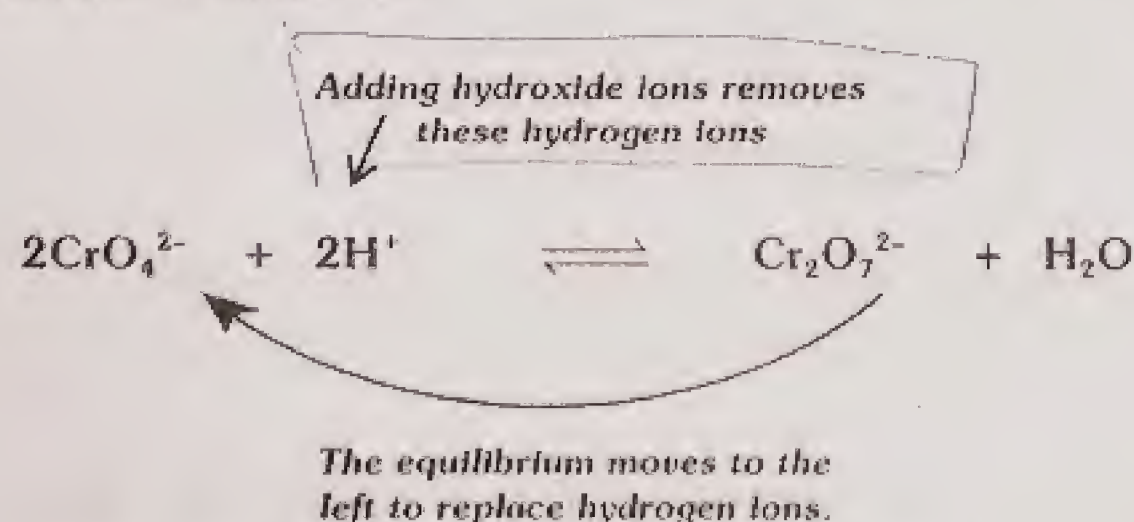
(viii) What are advantages of Potassium dichromate in titrations?

- Potassium dichromate (VI) can be used as a primary standard. It means that its stable solution of accurately known concentration can be directly prepared by weighing it.
- Potassium dichromate (VI) can be used in the presence of chloride ions. It is possible if chloride ions are not present in very high concentration. Thus, no unwanted side reactions occurs.

(ix) How does dichromate ion converted into chromate ions.

- The equilibrium reaction of the interconversion is:  

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$
- If hydroxide ions are added to this equilibrium, these react with the hydrogen ions. Thus, according to Le-Chatlier's principle, the equilibrium shifts to the left to replace them. Hence, dichromate ions are converted into chromate ions.



*Hydroxide ion*

**Q3: Give detailed answers for the following questions.**

(I) (a) What is the valence shell configuration of transition elements? How does it affect the following properties?

(i) Binding energy (ii) Paramagnetism (iii) oxidation states  
See Page 69, 70

(b) What are typical and non-typical transition elements?  
See Page 67

(c) Explain catalytic Activity of transition elements.  
See Page 71

(d) Write composition, properties and uses of: Brass, Bronze and Nichrome alloys.  
See Page 72

(II) (a) Explain different types of ligand with examples

(b) Describe the rules for naming the coordination complexes with examples.  
See Page 76

(III) (a) Explain shapes and origin of colors of coordination compounds.  
See Page 74

(b) Relate the coordination number of ions to the crystal structure of the component of which they are a part.



(a) Write systematic names to following complexes.

- |   |  |
|---|--|
| (i) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$               | Hexaamminecobalt (III) chloride            |
| (ii) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$             | Hexaaquoferron (II) ion                    |
| (iii) $\text{Na}_2[\text{CoF}_6]$                         | Sodium hexafluorocobaltate (II)            |
| (iv) $[\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3]$     | Triaquothydroxochromium (III)              |
| (v) $\text{K}_2[\text{PtCl}_6]$                           | Potassium hexachloroplatinate (IV)         |
| (vi) $[\text{Pt}(\text{OH})_2(\text{NH}_3)_4]\text{SO}_4$ | Tetraamminedihydroxoplatinum (IV) sulphate |
| (vii) $\text{K}_2[\text{Cu}(\text{CN})_4]$                | Potassium tetracyanocuprate (II)           |
| (viii) $\text{Na}_2[\text{NiCl}_4]$                       | Sodium tetrachloronickelate (II)           |
| (ix) $\text{Pt}(\text{NH}_3)_2\text{Cl}_4$                | Diamminetetrachloroplatinum (IV)           |
| (x) $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$                 | Diamminesilver (I) chloride                |

(b) Write chemical formulae of following complexes:

- |  |   |
|--|---|
| (i) Potassium hexacyanoferrate (II)          | $\text{K}_4[\text{Fe}(\text{CN})_6]$      |
| (ii) Sodium tetrachloronickelate (II)        | $\text{Na}_2[\text{NiCl}_4]$              |
| (iii) Tetrammine copper (II) Sulphate        | $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$   |
| (iv) Potassium hexachloroplatinate (IV)      | $\text{K}_2[\text{PtCl}_6]$               |
| (v) Dichlorotetragmine cobalt (III) Chloride | $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$ |

(c) Discuss vanadium (V) oxide as a catalyst with example.

See Page 84

(d) How does chromium (III) changes to chromium (VI)?

See Page 84

(e) Discuss potassium dichromate (VI) and Potassium manganate (VII) as an oxidizing agent in organic chemistry.

See Page 87



**TEST YOUR SKILLS**

Marks: 85

Time: 20 Minutes

**OBJECTIVE**

Marks: 17

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Q1. Circle the correct option i.e. A, B, C, D. Each part carries one mark.

- (i) Which is the general electronic configuration of d-block elements? ~~A~~  
A.  $(n-1)d^{1-4}ns^2$  B.  $(n-1)d^{1-10}ns^2$  C.  $(n-1)d^{1-10}ns^1$  D. All of the above
- (ii) The oxidation state of Mn in  $KMnO_4$  is ~~A~~  
A. +4 B. +2 C. +7 D. -7
- (iii) Which of the following does not show variable valency? ~~A~~  
A. Cr B. Zn C. Mn D. Fe
- (iv) Which of the following is paramagnetic? ~~A~~  
A.  $Mn^{2+}$  B.  $Fe^{3+}$  C.  $Fe^{2+}$  D. All of above
- (v) The hybridization of Cu in  $[Cu(NH_3)_4]^{2+}$  is ~~A~~  
A.  $sp^2$  B.  $dsp^2$  C.  $d^2sp^2$  D.  $d^2sp^3$
- (vi) Group VIB of transition elements contain  
A. Zn, Cd, Hg B. Fe, Ru, Os C. Cr, Mo, W D. Mn, Tc, Re
- (vii) The transition elements and their compounds are coloured due to splitting in ~~A~~  
A. d-orbital B. f-orbital C. s-orbital D. p-orbital
- (viii) The first transition series ends on the element ~~A~~  
A. Scandium B. Cadmium C. Zinc D. Mercury
- (ix) The oxidation state of Fe in  $K_4[Fe(CN)_6]$  is ~~A~~  
A. +3 B. +2 C. +1 D. +4
- (x) The shape of  $[Co(NH_3)_6]^{3+}$  is ~~A~~  
A. Tetrahedral B. Octahedral C. Square planar D. Pyramidal
- (xi) The strength of binding energy of transition elements depends upon ~~A~~  
A. number of electron pairs B. number of unpaired electron  
C. number of neutrons D. Number of protons
- (xii) If we add  $HNO_3$  to the original vanadium (II) solution, it produces ~~A~~  
A. blue ions B. green ions C. dull grey blue ions D. pink ions
- (xiii) All chromates are mostly ~~A~~  
A. White B. Yellow C. Red D. Green
- (xiv) The oxidation of  $CH_3OH$  is carried out with which of the following catalysts. ~~A~~  
A.  $ZnO + MnO_2$  B.  $MnO_2 + Cr_2O_3$  C.  $ZnO + CrO_3$  D.  $ZnO + Cr_2O_3$
- (xv) Acidified  $KMnO_4$  acts as ~~A~~  
A. reducing agent B. Oxidizing agent C. Dehydrating agent D. all of these
- (xvi) Brass alloy contains which of the following elements ~~A~~  
A. Cu, Sn B. Cu, Zn C. Sn, Zn D. Mn, Cu
- (xvii) Iron is used as a catalyst in: ~~A~~  
A. Birkland Process B. Contact Process C. Haber Process D. both b and c

**SUBJECTIVE**

Time: 2:35 Hours

Total Marks Section B and C: 68

Section - B (Marks 42) (14 × 3 = 42)

Q2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines.

- (i) a. What is Paramagnetism? 02  
b. What is the cause of Paramagnetism? 01
- (ii) a. How does vanadium can be oxidized from V(II) to V(III) by hydrogen ions? Give one equation. 02  
c. Give confirmatory test for  $Fe^{+3}$  ions? 01
- (iii) Name the following co-ordination compounds. 03  
a.  $K_4[Fe(CN)_6]$  b.  $[CoBr(NH_3)_5]SO_4$  c.  $[CrH_2O_4]([NH_4])_3$
- (iv) a. What are Complexes 01  
b. Write the systematic name of the complex  $K_2[PtCl_4]$  01  
c. Why  $Fe^{3+}$  ions do not exist in solution? 01
- (v) a. How is chromate ion ( $CrO_4^{2-}$ ) converted into dichromate ion ( $Cr_2O_7^{2-}$ ) and vice versa? 02
- (vi) a. Draw the geometric shape of co-ordination number 4 complexes 02  
b. Why transition elements shows variable oxidation state? 01



**14. d and f-Block Elements: Transition Elements**

1. What are transition elements? 01
2. Why is there a deviation in the electronic configuration of Cr and Cu? 02
3. What is meant by typical and non-typical transition elements? 1.5
4. Explain m.p. and b.p. increase upto the middle of transition series and then decrease? 1.5
5. In transition elements atomic size decreases at beginning then become almost constant and then increases at the end. Why? 02
6. What is the trend of Paramagnetism in transition metal series? 01
7. How colours are developed in complexes of transition metal series? 02
8. What is difference between paramagnetic and diamagnetic substances? 01
9. Why alloys are prepared? 01
10. What are substitutional alloys? Why transition metals form substitutional alloys? 02
11. Coordination compounds are very important. 01
12. What are coordination compounds? 01
13. What is a ligand? 01
14. What are polydentate ligands? Give examples? 01
15. What is coordination sphere? 01
16. What is coordination number? 01
17. How charge is calculated on central atom in coordination sphere? Give an example. 01
18. What is the relationship between magnetic moment and number of unpaired electrons? 01
19. How vanadium(V) is reduced to vanadium(II) by  $\text{H}^+$  ions? 02
20. How  $\text{KMnO}_4$  oxidizes vinyl benzenes? 1.5
21. Give confirmatory test of  $\text{Fe}^{3+}$  ions. 1.5
22. What is the general valence shell configuration of transition elements? 1.5
23. Differentiate between ferromagnetism and paramagnetism? 1.5
24. What is the composition of Bronze alloy? 01
25. Under what conditions Aluminium metal corrode? 01
26. Give units of magnetic moment? 01
27. Define 03
- a. co-ordination sphere      b. co-ordination number      c. central metal ion
28. (4) In which titration end point is clear potassium dichromate or potassium manganate 03

**Section - C**

**Note:** Attempt any TWO questions. All questions carry equal marks. ( $2 \times 13 = 26$ )

- Q. 3. a. How does ammonia react with hexaaquacopper(II) ions? 04
- b. When copper ion reacts with carbonate. Which types of precipitate are formed? 03
- c. What are the use of potassium permanganate in organic chemistry? 06
- Q. 4. a. How does hexaaquamanganese(II) reacts with the following? 04
- (i) hydroxide ions      (ii) ammonia solution
- b. What is geometry of the following complexes/compounds? 06
- (i)  $[\text{MnCl}_4]^{2-}$       (iii)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$       (iv)  $[\text{Co}(\text{NH}_3)_6]^{3+}$
- c. How does iron acts as a catalyst in the reaction between persulphate ions and iodide ions? 03
- Q. 5. a. Explain catalytic Activity of transition elements. 04
- b. What is a ligand? What are its types? 04
- c. Write IUPAC names of the following 05
- (i)  $\text{K}_4[\text{Fe}(\text{CN})_6]$       (ii)  $[\text{PtCl}_2(\text{NH}_3)_4]\text{SO}_4$       (iii)  $[\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3]$
- (iv)  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$       (v)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$



## CHAPTER # 15

# ORGANIC COMPOUNDS



There are many classes of chemical compounds, inorganic and organic. They are classified on the basis of source from which they were derived.

### Inorganic Compounds

The compounds which were of mineral origin were known as inorganic.

Examples: Salt, oil, marble, carbon dioxide etc.

### Organic Compounds

The compounds which were of vegetable or animal origin were called organic.

Examples: Wine, oil, sugar, vinegar, alcohol from wine, tartaric acid, sugar, glucose etc.

### Organic Chemistry

Organic chemistry is the chemistry of compound of carbon as carbon is the essential element in all organic compounds.

Organic chemistry is concerned with the chemistry of living material or substances which were at one time alive. It is therefore concerned with living plants or animals or substances like coal and oil which are derived from living plants, coral, or other microscopic sea organisms (oil).

### Modern Definition of Organic Chemistry:

Organic chemistry is that branch of chemistry which deals with the study of compounds of carbon and hydrogen (Hydrocarbons) and their derivatives.

### Exceptions to the definition of Organic Chemistry

There are several compounds which contain carbon and are not included in organic compounds.

Examples: carbon monoxide ( $\text{CO}$ ), carbon dioxide ( $\text{CO}_2$ ), carbon disulphide ( $\text{CS}_2$ ), carbonates ( $\text{CO}_3^{2-}$ ), bicarbonates ( $\text{HCO}_3^-$ ), Cyanides ( $\text{CN}^-$ ), thiocyanates ( $\text{SCN}^-$ ) etc.

These are studied in inorganic chemistry because of their properties.

### Exercise Q3 (1) What are the main sources of organic compounds?

## SOURCES OF ORGANIC COMPOUNDS

### Fossil Fuels

The dead remains of living organisms are called fossil remains.

The main sources of organic compounds are coal, petroleum and natural gas. These are called fossil fuels. It is because they are formed from fossil remains.

### (1) COAL

- Coal is the major source of organic compounds.
- It yields coke and coal-tar on pyrolysis or destructive distillation.
- More than 200 organic compounds have been directly isolated from coal-tar.
- These coal-tar products form the starting materials for the manufacture of thousands of useful aromatic compounds.



## 2) PETROLEUM

- In some parts of the world, a black thick sticky liquid seeps out of the ground. This liquid is called petroleum or Crude Oil.
- Petroleum is a complex mixture of hydrocarbons whose composition varies according to its place of occurrence.

### Points to Remember

Important products prepared from petroleum

Methane ( $\text{CH}_4$ )

Ethylene ( $\text{CH}_2=\text{CH}_2$ )

Acetylene ( $\text{HC}\equiv\text{CH}$ )

Propene ( $\text{CH}_3\text{CH}=\text{CH}_2$ )

Benzene ( $\text{C}_6\text{H}_6$ )



Toluene ( $\text{C}_6\text{H}_5\text{CH}_3$ )

Xylene ( $\text{C}_6\text{H}_4(\text{CH}_3)_2$ )

## 3) NATURAL GAS

- It is mixture of low boiling hydrocarbons.
- Major portion of the natural gas is methane ( $\text{CH}_4$  about 85%).
- Other gases include ethane, propane and butane. It formed by the decomposition of organic matter.
- In Pakistan, there are vast reserves of gas in Sui in Baluchistan, Sind and Punjab.

## 4) PLANTS

Many organic compounds are obtained directly from plant or animal sources by suitable methods of isolation.

### Examples:

Carbohydrates (cellulose, sugars, starches), proteins (silk, wool, casein, food proteins, fats and oils from seed, soybeans, oils, lard, butter), alkaloids (quinine, morphine, strychnine), hormones, vitamins, perfumes, flavors, resins.

## PARTIAL AND TOTAL SYNTHESIS

The process in which compounds isolated from natural sources (e.g. plant material or coal or petroleum etc.) are used as starting materials to produce other organic molecules is called partial synthesis.

The process in which an organic molecule is synthesized from small and cheap readily available molecules is called total synthesis.

- Simple organic compounds derived from petroleum or coal has been converted into thousands of useful materials by synthetic methods.
- Synthetic organic chemistry is related to almost every phase of life.

### Examples:

- Many synthetic organic compounds have replaced the compounds from natural sources. e.g., dyes, rubber, fibers plastics, drugs, vitamins.
- In many cases the synthetic materials are superior to the natural compounds replaced. e.g., synthetic dyes are superior to those of natural origin.
- In other cases the synthetic material are entirely unknown in nature and fill the requirements not satisfied from any other source. e.g., ether, glycol, mercurochrome, aspirin, and the sulpha drugs.

## FERMENTATION

Fermentation is defined as the production of chemicals by the action of micro-organisms.

By employing appropriate organism hosts, useful substances are produced including alcohols, acids, vitamins and antibiotics.

## QUICK QUIZ-1

(1) Define modern definition of organic chemistry?

Organic chemistry is that branch of chemistry which deals with the study of compounds of carbon and hydrogen (hydrocarbons) and their derivatives.



**(2) Enlist different sources of organic compounds**

- The main sources of organic compounds are coal, petroleum and natural gas. These are called fossil fuels.
- Many organic compounds are also obtained directly from plants or animals.

**(3) Write important products from petroleum.**

Important products prepared from petroleum

Methane ( $\text{CH}_4$ ).

Ethylene ( $\text{CH}_2=\text{CH}_2$ ).

Acetylene ( $\text{HC}\equiv\text{CH}$ ).

Propene ( $\text{CH}_3\text{CH}=\text{CH}_2$ )

Benzene  $\text{C}_6\text{H}_6$ , 

Toluene  $\text{C}_6\text{H}_5\text{CH}_3$ .

Xylene  $\text{C}_6\text{H}_4(\text{CH}_3)_2$

**(4) What are alkaloids?**

Alkaloids are a group of naturally occurring organic compounds which are mostly nitrogen-containing bases.

e.g. quinine, morphine, strychnine

However, some alkaloids are neutral and some alkaloids having similar structure to the natural alkaloids have been synthesized in laboratory as well.

**(5) Define fermentation?**

Fermentation is defined as the production of chemicals by the action of micro-organism.

By employing appropriate organism hosts, useful substances are produced including alcohols, acids, vitamins and antibiotics.

## COAL (AS A SOURCE OF ORGANIC COMPOUND)

- Coal is produced by the decaying of trees buried under the earth crust under the influence of temperature and pressure. These trees got converted into coal.
- The total coal reserves of Pakistan are estimated by the geological survey of Pakistan to be 184 billion tones

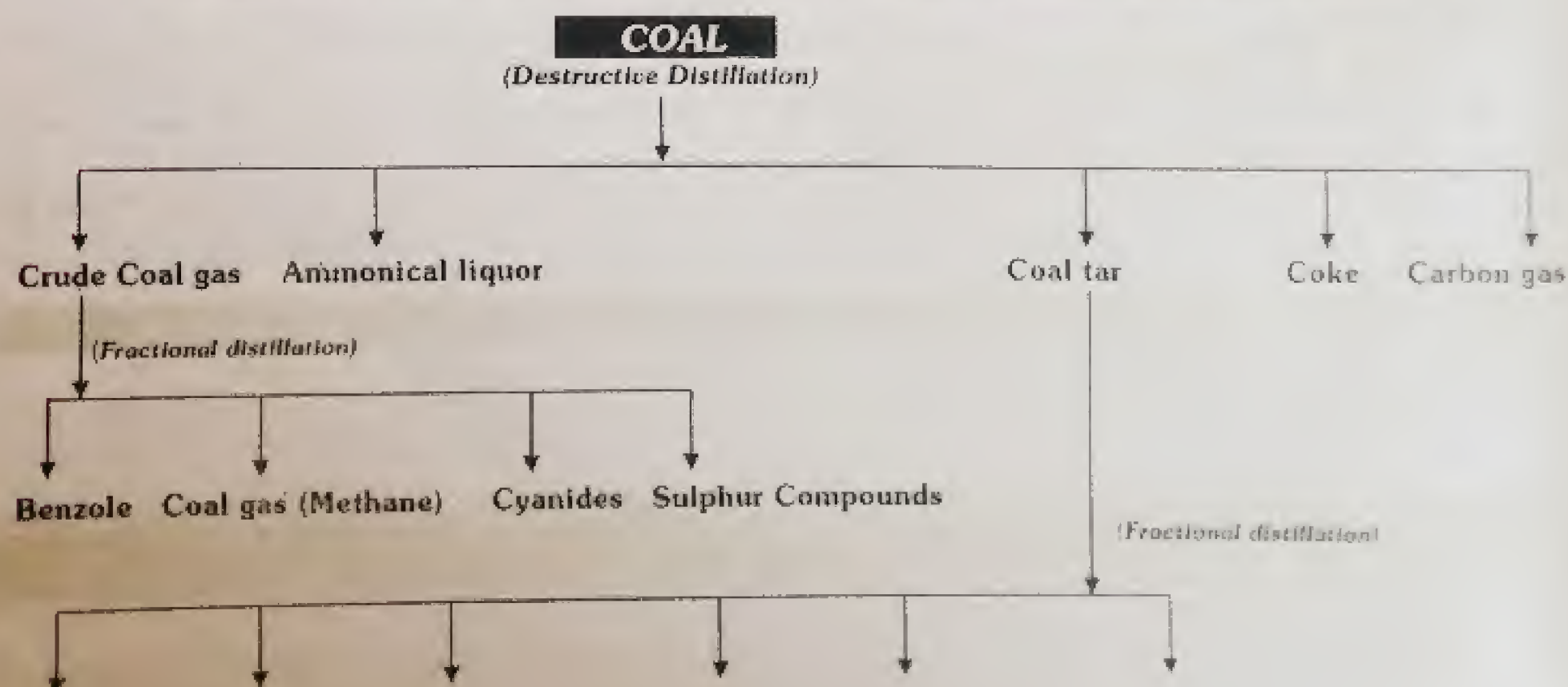
### DESTRUCTIVE DISTILLATION OF COAL:

The distillation carried out in the absence of air is called destructive distillation.

**Process**

- When coal is heated in the absence of air (temperature ranging from  $500-1000^\circ\text{C}$ ); it is converted into coke coal gas and coal tar.
- Coal tar contains a large number of organic compounds which separate out on fractional distillation.

The separation of liquids on the basis of their boiling points is called fractional distillation.





## CHARACTERISTICS OF ORGANIC COMPOUNDS

**Exercise Q3 (II) Write down the characteristics of organic compound from inorganic compounds.**

Organic compounds have entirely different properties from inorganic compounds. Some of their general properties are described below:

**1. Composition**

Carbon is an essential constituent of all organic compounds.

**2. Combustion**

Organic compounds with high percentage of carbon are generally combustible in nature.

**3. Melting and Boiling Points**

Organic compounds generally have low melting and boiling points and are volatile in nature.

**4. Solubility**

Organic compounds with non-polar linkages are generally soluble in organic solvents such as alcohol, ether, benzene, etc. They are less soluble in water.

**5. Stability**

Since organic compounds have low melting and boiling points, they generally decompose at high temperature into simple substances.

**6. Electrical Conductivity**

Due to the presence of covalent bonds, organic compounds are poor conductor of electricity both in fused state and in solution form.

**7. Source**

Most of organic compounds are obtained from plants and animal sources.

**8. Rate of Reaction**

Their rates of reaction are very slow and need specific conditions.

## QUICK QUIZ-2

**(1) What is coal?**

It is a black colour mineral. Coal is produced by the decaying of trees buried under the earth crust under the influence of temperature and pressure. These trees got converted into coal.

**(2) What are the products of fractional distillation of coal tar?**

Benzene, Toluene, Xylene, Naphthalene, Phenols and many other compounds.

**(3) What we obtain by fractional distillation of coal gas?**

Benzole, Coal gas (Methane), Cyanides, Sulphur Compounds.

**Exercise Q3 (III) How organic compounds are used in our daily life?**

## USES OF ORGANIC COMPOUNDS

No field of science is so closely related with our daily activities as is organic chemistry.

- The food is mainly organic in nature.
- The food undergoes changes in our bodies which are organic chemical reactions.
- Metabolism, growth and maintenance of our bodily functions involve organic chemistry. Similar is the case with all changes taking place throughout the entire living world, plant and animal.



- The clothes, the dyes to color them, the soap and starch to launder them are products of organic chemical industry.
- The leather of shoes as well as the dye and shoe polish are also products of organic chemical industry.
- Many of the structural materials in our houses are organic. These include furniture, as well as the paints and varnishes used for finishing them etc.
- Many of the equipments in our motor cars, their fuel and lubricants are organic.
- The fuels which power industrial plants are also organic in nature.

A list of important use of organic compounds is given below

1. **Food:** Proteins, fats, carbohydrates, oils
2. **Clothing:** (Cotton, silk, wool, nylon, rayon, Dacron)
  - The natural fiber like cotton, silk and wool have plant and animal origin.
  - Synthetic fiber like rayon, Dacron and nylon are prepared in the industry.
3. **Shelter:** (Wood, paints, varnishes)
4. **Power and Transportation:** (Natural gas, petroleum products, coal)  
Natural gas, petroleum and gas used for power and transportation are organic substances.
5. **Medicines and Drugs:** (Penicillin, streptomycin)  
All types of the medicines used in the allopathy, homeopathy and ayurveda involve the organic compounds.
6. **Insecticides:** Insecticides like DDT, which are being widely used are organic substances.
7. **Hormones and Steroids:** Hormones and steroids are complex organic compounds.
8. **Vitamins and Enzymes:** All the vitamins which are dietary factors are organic compounds. Similarly enzymes are organic substances.
9. **Antiseptics and Anesthetics:** These are the families of the medicines and are organic in nature.
10. **Pigments and Dyes:** Pigments and dyes are used for paints and clothes and are organic in nature.
11. **Paper and Inks:** Paper and inks are the sources of civilization and organic materials.
12. **Perfumes and Flavors:** Perfumes and flavors and all cosmetics are organic in nature.
13. **Plastics, Rubbers, and Resins:** Plastics, rubber and resins are organic in nature.
14. **Propellants and Explosives:** Propellants, explosives and refrigerants are well-known organic materials.
15. **Soaps and Detergents:** Soaps and detergent are organic compounds.
16. **Herbicides:** Treflan
17. **Photographic films and Developers**
18. **Biological Problems and Organic Chemistry:**  
Most of the biologic problems are concerned with organic chemistry.  
e.g. organic reactions are involved in formation of cancer and AIDS. These changes happen in metabolism and growth process etc.

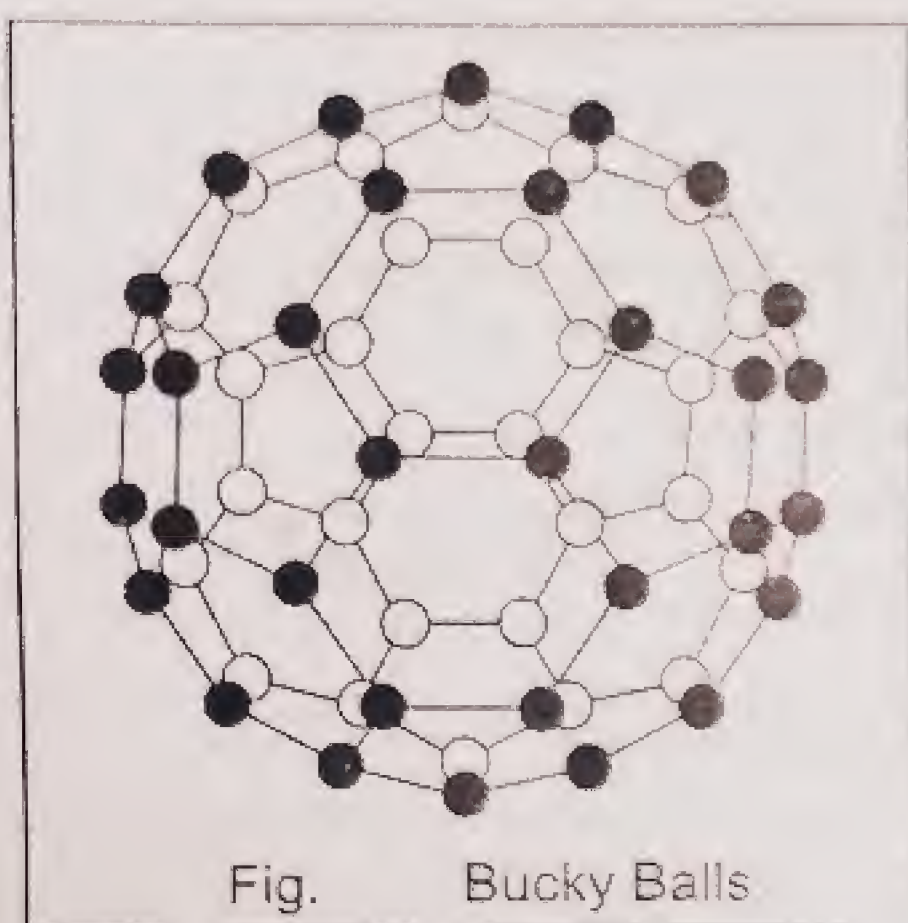


## NEW ALLOTROPES OF CARBONS: BUCKY BALLS

- In 1985, a new group of allotropic forms of carbon, was discovered called Bucky Balls.
- The full name of Bucky Balls is Buckminster Fullerene.
- Scientists named it after an architect Buckminster, who designed a Bucky ball shaped building in Montreal.
- Bucky balls are used as semi-conductors and lubricants.

### Structure of Bucky Balls

- These have carbon atoms ranging from forty to hundred. The carbon atoms are arranged in a hollow cage like structure. They are called Bucky Balls.
- The simplest of them is  $C_{60}$  and its molecule is made up of sixty carbon atoms.
- The carbon atoms fold around and make a ball shaped molecule.
- The new molecule looks just like a football. The carbon atoms join together to form pentagon and hexagon structures.



## QUICK QUIZ-3

### (1) What are allotropes?

An element may exist in different crystalline forms. These forms are called Allotropes and the phenomenon is called allotropy.

- e.g. (i) C (as diamond) \_\_\_\_\_ in cubic form.  
 (ii) C (as graphite) \_\_\_\_\_ in hexagonal form.

### (2) Define the third allotropic form of carbon.

- In 1985, a new group of allotropic forms of carbon was discovered called Bucky balls.
- The full name of Bucky Balls is Buckminster Fullerene.
- Scientists named it after an architect Buckminster, who designed a Bucky ball shaped building in Montreal.

### (3) Why it was given the name Bucky balls?

- Scientists named Bucky balls after an architect Buckminster, who designed a Bucky ball shaped building in Montreal.



## FUNCTIONAL GROUPS AND HOMOLOGOUS SERIES

**Exercise Q1 (b)** Write down any ten functional groups of organic compounds? Give reasons for their importance of organic chemistry.

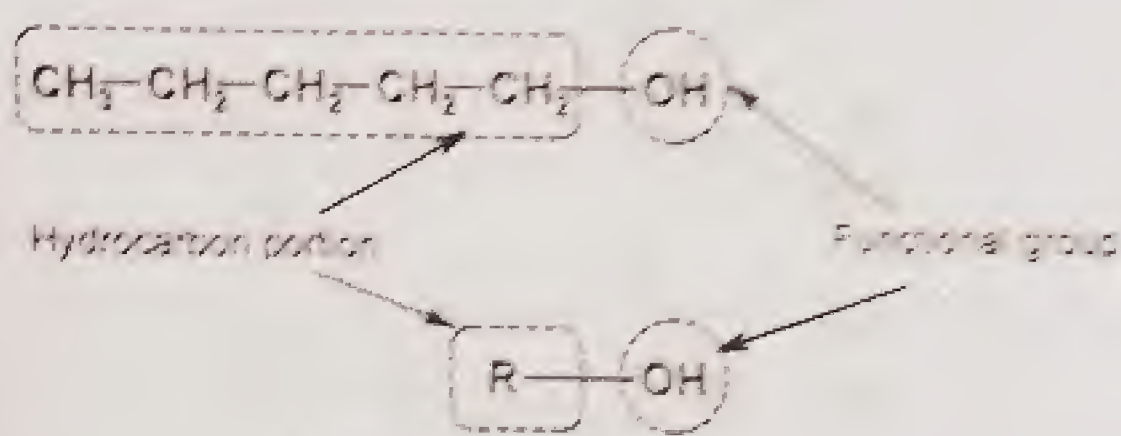
### FUNCTIONAL GROUP

A functional group is an atom or group of atoms in a molecule that gives the molecule its characteristic chemical properties.

- Several transformations of organic molecules are carried out. In most cases the change will occur at one "spot" in the original reacting molecule. This spot is the functional group.
- A molecule can contain more than one functional group. It is then said to be **Polyfunctional** and the properties of each functional group may be modified by the presence of the others.

**Examples:**

Double bond, triple bond,  $-Cl$ ,  $-Br$ ,  $-CH_3$ ,  $-NH_2$  groups etc.



R is defined as alkyl group

- The symbol R- is used to represent the hydrocarbon portion to which the functional group is attached. Thus R- can be  $CH_3-$ ,  $CH_3CH_2-$ ,  $(CH_3)_3CH-$  or any other group of C and H atoms with one free valence by which the functional group is attached.
- The functional group is the action group of a molecule. The hydrocarbon portion remains inert.
- Each functional group undergoes characteristic reactions. By recognizing the functional group in a molecule, it is possible to predict the reactions which that molecule will undergo.

**Importance:**

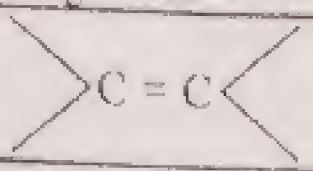

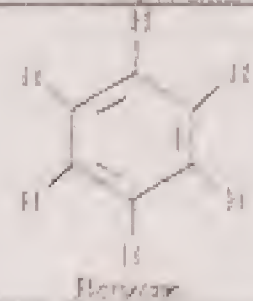
The concept of functional group is important to organic chemistry for three reasons:

- (1) Functional groups serve as basis for nomenclature (naming) of organic compounds.
- (2) Functional groups serve to classify organic compounds into classes/families. All compounds with the same functional group belong to the same class.
- (3) A functional group is a site of chemical reactivity in a molecule. Compounds in the same class have similar chemical properties.

**Remember!** Abbreviations for common Alkyl/Aryl groups. These are to be used in next reactions  
Methyl (**Me**), Ethyl (**Et**), n-Propyl (**n-Pr**), isopropyl (**iso-Pr**), Phenyl (**Ph**) etc.



Following is the list of some common functional groups.  
Some functional groups:

Family	Structure of functional group	Simple example
Alkane	Containing only C - H and C - C single bond	$\text{CH}_3 - \text{CH}_3$ Ethane
Alkene		$\text{H}_2\text{C} = \text{CH}_2$ Ethene
Alkyne	$-\text{C} \equiv \text{C}-$	$\text{H} - \text{C} \equiv \text{C} - \text{H}$ Ethyne
Arene		 Benzene
Halide	$\begin{array}{c}   \\ -\text{C}-\ddot{\text{X}}: \\   \end{array}$ (X = F, Cl, Br, I)	$\text{H}_3\text{C}-\ddot{\text{Cl}}:$ Methyl chloride (Gujranwala 2004)
Alcohol	$\begin{array}{c}   \\ -\text{C}-\ddot{\text{O}}-\text{H} \\   \end{array}$	$\text{H}_3\text{C}-\ddot{\text{O}}-\text{H}$ Methyl alcohol
Ether	$\begin{array}{c}   \quad   \\ -\text{C}-\ddot{\text{O}}-\text{C}- \\   \quad   \end{array}$	$\text{H}_3\text{C}-\ddot{\text{O}}-\text{CH}_3$ Dimethyl ether
Amine	$\begin{array}{c}   \quad   \quad   \\ -\text{C}-\ddot{\text{N}}-\text{H}, -\text{C}-\ddot{\text{N}}-\text{H} \\   \quad   \quad   \\ \text{H} \\   \\ -\text{C}-\ddot{\text{N}}- \\   \quad   \end{array}$	$\text{H}_3\text{C}-\ddot{\text{N}}\text{H}_2$ Methyl amine
Nitrile	$\begin{array}{c}   \\ -\text{C}-\text{C} \equiv \text{N}: \\   \end{array}$	$\text{H}_3\text{C}-\text{C} \equiv \text{N}$ Methyl cyanide (methyl nitrile)
Nitro	$\begin{array}{c}   \quad + \quad \ddot{\text{O}} \\ -\text{C}-\text{N} \quad \nearrow \\   \quad \searrow \quad \ddot{\text{O}}^- \end{array}$	$\text{H}_3\text{C}-\text{N} \begin{array}{l} \nearrow \text{O}^+ \\ \searrow \text{O}^- \end{array}$ Nitromethane
Sulphide	$\begin{array}{c}   \quad   \\ -\text{C}-\ddot{\text{S}}-\text{C}- \\   \quad   \end{array}$	$\text{H}_3\text{C}-\text{S}-\text{CH}_3$ Dimethyl sulphide
Sulphoxide	$\begin{array}{c} \quad \ddot{\text{O}}^- \\ \quad \uparrow \\   \quad \text{S} \quad   \\ -\text{C}- \quad -\text{C}- \\   \quad   \end{array}$	$\begin{array}{c} \text{O}^+ \\ \uparrow \\ \text{H}_3\text{C}-\text{S}^+-\text{CH}_3 \end{array}$ Dimethyl sulfoxide



Sulphonic	$\begin{array}{c} \text{O}^- \\   \\ -\text{C}-\text{S}^+(\text{O})_2-\text{C}- \\   \quad   \\ \text{O}^- \quad \text{O}^- \end{array}$	$\begin{array}{c} \text{O}^- \\   \\ \text{Cl}_3\text{C}-\text{C}^+(\text{O})-\text{Cl}_3 \\   \\ \text{O}^- \end{array}$ Trichloromethyl sulphonic
Amide	$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{N}-\text{H} \\   \end{array}$	$\text{H}_3\text{C}-\text{N}-\text{H}$ Methylamine
Carbonyl	$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{C}- \\   \end{array}$	Addition, various, and derivatives of acids
Aldehyde	$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{C}-\text{H} \\   \end{array}$	$\begin{array}{c} \text{O} \\    \\ \text{H}_3\text{C}-\text{C}-\text{H} \end{array}$ Acetaldehyde (Gujaratwala 1984)
Ketone	$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{C}-\text{C}- \\   \quad   \end{array}$	$\begin{array}{c} \text{O} \\    \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{Cl}_3 \\   \quad   \end{array}$ Acetone (Gujaratwala 1984)
Carboxylic Acid	$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{C}-\text{O}-\text{H} \\   \end{array}$	$\begin{array}{c} \text{O} \\    \\ \text{H}_3\text{C}-\text{C}-\text{O}-\text{H} \end{array}$ Acetic acid (Gujaratwala 1984)
Ester	$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{C}-\text{O}-\text{C}- \\   \quad   \end{array}$	$\begin{array}{c} \text{O} \\    \\ \text{H}_3\text{C}-\text{C}-\text{O}-\text{C}-\text{Cl}_3 \\   \quad   \end{array}$ Methyl benzoate
Amide	$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{C}-\text{N}-\text{H} \\   \end{array}$	$\begin{array}{c} \text{O} \\    \\ \text{H}_3\text{C}-\text{C}-\text{N}-\text{H} \end{array}$ Acetamide (Gujaratwala 1984)
Carboxylic chloride	$\begin{array}{c} \text{O} \\    \\ -\text{C}-\text{C}-\text{Cl} \\   \end{array}$	$\begin{array}{c} \text{O} \\    \\ \text{H}_3\text{C}-\text{C}-\text{Cl} \end{array}$ Acetyl chloride
Carboxylic anhydride	$\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ -\text{C}-\text{C}-\text{O}-\text{C}-\text{C}- \\   \quad   \end{array}$	$\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ \text{H}_3\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{Cl}_3 \\   \quad   \end{array}$ Acetic anhydride



## HOMOLOGOUS SERIES

A homologous series is a series of compound in which adjacent members differ by a  $\text{CH}_2$  unit. The individual members are called Homologs.

Example:

Alcohol series: The general formula is  $\text{R-OH}$  or  $\text{C}_n\text{H}_{2n+2}\text{O}$

The homologous series of alcohol can be represented as:

n	R	Formula
1	$\text{CH}_3-$	$\text{CH}_3\text{OH}$
2	$\text{CH}_3\text{CH}_2-$	$\text{CH}_3\text{CH}_2\text{OH}$
3	$\text{CH}_3\text{CH}_2\text{CH}_2-$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
4	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$

### General Characteristics of a Homologous Series

- (1) All compounds in the series contain the same elements and the functional group.
- (2) All compounds in the series can be represented by a general formula.
- (3) The molecular formula of each homolog differs from one above and one below it by a  $\text{CH}_2$  unit.
- (4) All compounds in the series can be prepared by similar methods.
- (5) All compounds in the series have similar chemical properties.
- (6) There is a gradual variation in physical properties with increasing molecular weight.

## QUICK QUIZ-4

(1) What are general formulas for alkanes, alkenes and alkynes?

Alkanes  $\text{C}_n\text{H}_{2n+2}$       Alkenes  $\text{C}_n\text{H}_{2n}$       Alkynes  $\text{C}_n\text{H}_{2n-2}$

(2) What are homologs?

A homologous series is a series of compound in which adjacent members differ by a  $\text{CH}_2$  unit. The individual members are called Homologs.

(3) Why we arrange compounds in homologous series?

The large number of organic compounds is classified into few homologous series. Thus their study becomes easier due to following reasons:

- All compounds in the series can be prepared by similar methods.
- All compounds in the series have similar chemical properties.
- There is a gradual variation in physical properties with increasing molecular weight.

Exercise Q3 (v) Give the chemical tests for the detection of elements in organic compounds.

## DETECTION OF ELEMENTS IN ORGANIC COMPOUNDS

- Carbon is an essential constituent of all organic compounds.
- Hydrogen is also present in almost all organic compounds.
- Some organic compounds may contain Nitrogen, Sulphur, and Halogen, Oxygen, Phosphorus and Metals.

### (A) DETECTION OF CARBON AND HYDROGEN:

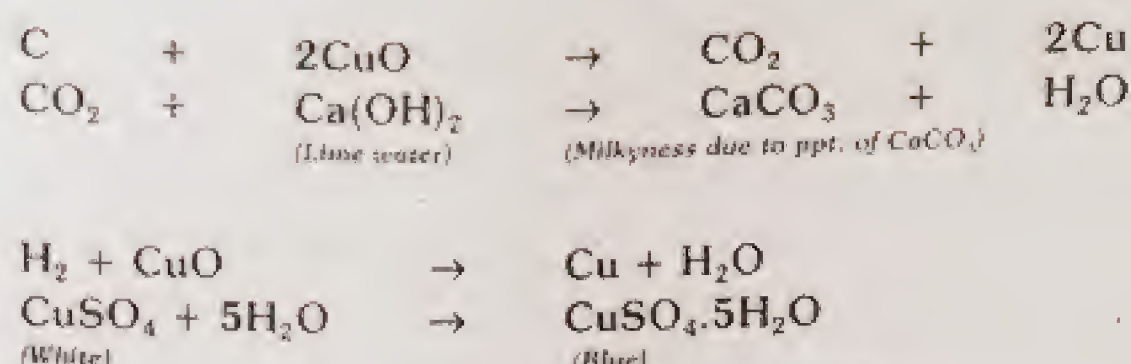
Method

- A small amount of organic compound is heated with  $\text{CuO}$  in a glass test tube as shown in the figure.
- On heating the mixture carbon and hydrogen are oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  respectively.
- $\text{CO}_2$  turns lime water milky which proves the presence of carbon.
- The water vapour from white anhydrous copper sulphate blue.





**Reactions**

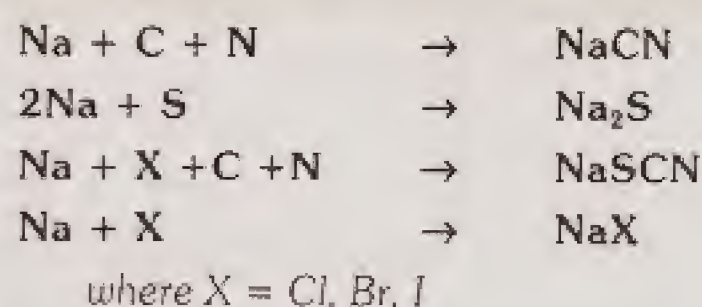


**(B) DETECTION OF NITROGEN, SULPHUR AND HALOGENS**

Preparation of Lassaigne's Solution/Sodium Extract

- (1) Cut a small piece of sodium metal with the help of knife
- (2) Put this piece of sodium metal in a fusion tube.
- (3) Heat the fusion tube in a flame to melt sodium metal.
- (4) When sodium metal is melted, then add a small amount of powdered organic compounds into fusion tube.
- (5) Then heat fusion tube in flame till its bottom become red hot.
- (6) Break this fusion tube in a china dish containing 20cm<sup>3</sup> of distilled water.
- (7) Mix, boil and then filter the solution.
- (8) The filtrate obtained is called Lassaigne's solution or sodium extract.
- (9) Divide this filtrate into three portions and test the presence of N, S and (X) halogens respectively.

**Reactions (Chemistry of Preparation of Lassaigne's solution):**



The tests for nitrogen, sulphur and halogens are performed with Lassaigne's filtrate.

**TEST FOR NITROGEN:**

**Method**

- To one portion of Lassaigne's filtrate a few drops of NaOH is added to make it alkaline and then then freshly prepared ferrous sulphate (FeSO<sub>4</sub>) solution is added to it.
- The solution is boiled and a few drops of FeCl<sub>3</sub> solution and HCl are added to it.
- The appearance of blue or greenish blue (Prussian blue) color or ppt. proves the presence of nitrogen in the organic compound.

**Reactions**



**Note:**

- If a blood red color is produced instead of Prussian blue color then it proves that nitrogen and Sulphur both are present in the organic compound.



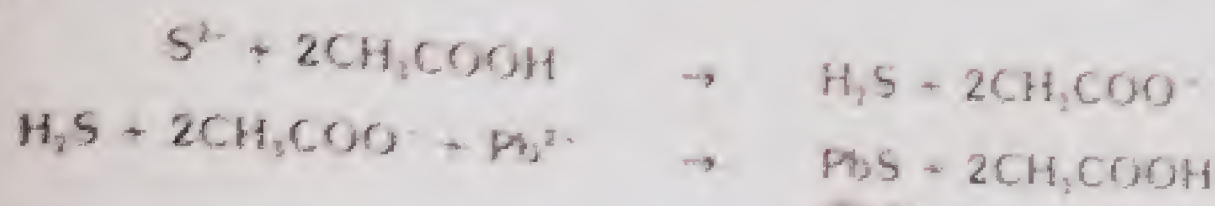


## TEST FOR SULPHUR:

### Method

- Another portion of Lassaigne's filtrate is acidified with acetic acid.
- The solution is boiled to expel  $\text{H}_2\text{S}$  gas.
- The  $\text{H}_2\text{S}$  gas turns lead acetate paper black that indicates the presence of Sulphur in the compound.

### Reactions



## TEST FOR HALOGENS

### Sodium Test

- A third portion of Lassaigne's solution is boiled with nitric acid to expel cyanide ion and sulphide ion.
- Then  $\text{AgNO}_3$  solution is added to the solution.
- The formation of precipitate shows the presence of a halogen.
  - ✓ a white ppt. soluble in  $\text{NH}_4\text{OH}$  shows the presence of chloride.
  - ✓ a pale yellow ppt. partially soluble in  $\text{NH}_4\text{OH}$  shows the presence of bromide.
  - ✓ a deep yellow ppt. insoluble in  $\text{NH}_4\text{OH}$  indicates iodine.



## C) DETECTION OF OXYGEN

- There is no conclusive test for oxygen.
- Its presence in organic compounds is often inferred by indirect methods.

### Test 1:

- The substance is heated alone in a dry test-tube, preferably in an atmosphere of nitrogen.
- Formation of droplets of water on cooler parts of the tube obviously shows the presence of oxygen.
- A negative result, however, does not necessarily show the absence of oxygen.

### Test 2:

- The second method is to test for the presence of various oxygen containing groups such as hydroxyl ( $\text{OH}$ ), carbonyl ( $\text{COOH}$ ), aldehyde ( $\text{CHO}$ ), nitro ( $\text{NO}_2$ ) etc.
- If any of these is detected, the presence of oxygen is confirmed.

### Test 3:

- The sure test for oxygen depends on the determination of the percentage of all other elements present in the given compound.
- If the sum of these percentages fall short of hundred the remainder gives the percentage of oxygen and thus confirms.

## D) DETECTION OF PHOSPHORUS

- The solid substance is heated strongly with an oxidizing agent such as concentrated nitric acid and mixture of sodium carbonate and potassium nitrate.
- The phosphorus present in the substance has oxidized to phosphate.
- The residue is extracted with water, boiled with some nitric acid.
- Then a hot solution of ammonium molybdate is added to it in excess.
- A yellow coloration of precipitate indicated the presence of phosphorus.

## E) DETECTION OF METALS

- The substance is strongly heated in a crucible, preferably of platinum, till all reaction ceases.
- An incombustible residue indicated the presence of a metal in the substance.
- The residue is extracted with dilute acid and the solution is test for the presence of metallic radical by the usual scheme employed for inorganic salts.



# **SCIENCE, TECHNOLOGY AND SOCIETY**

## **QUESTIONS (SHORT ANSWER TYPE AND LONG ANSWER)**

1. What is science?
2. Define technology. Give examples of technology.
3. How does science and technology affect society?
4. Give examples of science and technology.
5. How does science and technology affect society?

## **ANSWERS (SHORT ANSWER)**

1. Science is the study of the natural world and the laws that govern it.
2. Technology is the application of scientific knowledge to solve problems. Examples include computers, cars, and medicine.
3. Science and technology have both positive and negative impacts on society. Positive impacts include improved healthcare, communication, and transportation. Negative impacts include environmental pollution, job displacement, and privacy concerns.
4. Examples of science include physics, chemistry, biology, and earth science. Examples of technology include computers, smartphones, and the internet.
5. Science and technology have both positive and negative impacts on society. Positive impacts include improved healthcare, communication, and transportation. Negative impacts include environmental pollution, job displacement, and privacy concerns.



## **SOCIETY, TECHNOLOGY AND SCIENCE**

### **ORGANIC COMPOUNDS FROM PLANTS AND ANIMALS**

- Most sugar
- Some alkaloids (a naturally occurring nitrogenous organic molecule)
- Some terpenoids (a large class of natural products consisting of isoprene ( $C_5$ ) units)
- Certain nutrients e.g. vitamins
- Antigens, Carbohydrates, Hormones, Lipids and Fatty acids, fats and oils, Neurotransmitters, Nucleic acid, Proteins, Peptides and amino acids, Lectins (sugar-binding species)

### **DRUGS FROM PLANTS**

#### **Quinine**

An antimalarial and antipyretic medicine obtained from *Cinchona ledgeriana* (quinine tree).

#### **Nicotine**

An insecticide obtained from *Nicotiana tabacum* (tobacco).

#### **Menthol**

A rubefacient (a substance for topical application that causes dilation of the capillaries and an increase in blood circulation) obtained from *Mentha* species (mint).

#### **Camphor**

A rubefacient obtained from *Cinnamomum camphora* (camphor tree).

#### **Rutin**

Used for the treatment of capillary fragility; obtained from citrus species e.g. orange, grapefruit etc.

#### **Hesperidin**

Used for the treatment of capillary fragility; obtained from citrus species e.g. orange.

#### **Curcumin**

A choloretic; obtained from *Curcuma longa* (turmeric).

#### **Cocaine**

A local anaesthetic; obtained from *Erythroxylum coca* (coca plant).

#### **Caffeine**

A CNS stimulant; obtained from *Camellia sinensis* (tea, coffee and cocoa).

#### **Bromelain**

An anti-inflammatory drug; obtained from *Ananas comosus* (pineapple).



## EXERCISE

Q1: Select the right answer from the choices given with each question.

- The major portion of natural gas is  
(a) ethane (b) propane (c) butane (d) methane
- In organic compounds carbon atoms form  
(a) ionic bond (b) metallic bond (c) covalent bond (d) none of these
- Which of the following is an aromatic compound  
(a) Propanol (b) Cyclohexane (c) Benzene (d) Toluene
- There are a few homologous series of compounds. The existence of homologous series is due to  
(a) Functional group (b) Cracking (c) Isomerism (d) Polymerization
- Which of the following compound is heterocyclic?  
(a) Pyridine (b) Pyrene (c) Thiophene (d) H<sub>2</sub>O of the above
- Select from the following the one, which is alcohol  
(a)  $\text{CH}_3\text{CH}_2\text{OH}$  (b)  $\text{CH}_3\text{OCH}_3$  (c)  $\text{CH}_3\text{COOH}$  (d)  $\text{CH}_3\text{CH}_2\text{Br}$
- Lassaigne's solution is prepared in the detection of elements of organic compound. Which metal is used for the reaction with organic compound?  
(a) Aluminium (b) Sodium (c) Iron (d) Copper
- When  $\text{AgNO}_3$  is added to the Lassaigne's solution which colour is formed for iodine?  
(a) Blue (b) Violet (c) Green (d) Deep Yellow
- When water vapours are passed over white anhydrous copper sulphate, which colour is formed?  
(a) White (b) Deep blue (c) Yellow (d) Brown
- The simplest molecule of Bucky Ball contain carbon atoms  
(a) 20 (b) 8 (c) 60 (d) 100
- If a molecule contains more than one functional group, it is known as  
(a) Derivative (b) Polyfunctional (c) Heterocyclic (d) Isomer

## ANSWERS TO MULTIPLE CHOICE QUESTIONS

<b>(i) Ans: (d) methane</b> The natural gas contains about 85% methane.	<b>(ii) Ans: (c) covalent bond</b> In organic compounds carbon atoms shares 4 electrons with other atoms to form covalent bonds.
<b>(iii) Ans: (d) Benzene</b> By definition, benzene is an aromatic compound.	<b>(iv) Ans: (a) Functional group</b> All the members of a homologous series have same functional group, e.g. Alcohol series has OH functional group.
<b>(v) Ans: (a) Pyridine</b> It contains a nitrogen atom in the ring.	<b>(vi) Ans: (a) <math>\text{CH}_3\text{CH}_2\text{OH}</math></b> The functional group of alcohols is -OH.
<b>(vii) Ans: (b) Sodium</b> It is because, it is a very reactive metal.	<b>(viii) Ans: (d) Deep Yellow</b> Deep yellow ppt. of $\text{AgI}$ is produced.
<b>(ix) Ans: (b) Deep blue</b> Anhydrous $\text{CuSO}_4$ is white. When it absorbs water it becomes deep blue in colour due to formation of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .	<b>(x) Ans: (c) 60</b> The simplest Bucky ball is $\text{C}_{60}$ . i.e. it contains 60 carbon atoms.
<b>(xi) Ans: (b) Polyfunctional</b> By definition a compound with more than one functional group is called a polyfunctional compound.	<b>(xii) Ans:</b>
<b>(xiii) Ans:</b>	

Q2: Give brief answers for the following questions.

What is functional group?

A functional group is an atom or group of atoms in a molecule that gives the molecule its characteristic chemical properties.

A molecule can contain more than one functional group. It is then said to be Polyfunctional, and the properties of each functional group may be modified by the presence of the others.

Examples: Double bond, triple bond, -Cl, -Br, -OH, -NH<sub>2</sub> groups etc.



(ii) **What is the difference between partial and total synthesis of organic compounds?**

- The process in which compounds isolated from natural sources (e.g. plant material or coal or petroleum etc.) are used as starting materials to produce other organic molecules is called partial synthesis.

The process in which an organic molecule is synthesized from small and cheap readily available molecules is called total synthesis.

(iii) **How organic compounds are derived by fermentation process?**

Fermentation is defined as the production of chemicals by the action of micro-organisms.

By employing appropriate organism hosts of useful substances are produced including alcohols, acids, vitamins and antibiotics.

(iv) **What is coal? How is coal used as source of organic compounds?**

(v) **What is name of new allotropic form of carbon? Give its definition?**

In 1985, a new group of allotropic forms of carbon was discovered called Bucky balls.

These have carbon atoms ranging from forty to hundred. The carbon atoms are arranged in a hollow cage like structure. They are called Bucky Balls.

(vi) **What is Homologous series?**

A homologous series is a series of compound in which adjacent members differ by a  $\text{CH}_2$  unit. The individual members are called Homolog.

Example:

Alcohol series. Its general formula is  $\text{ROH}$  or  $\text{C}_n\text{H}_{2n+1}\text{OH}$

The homologous series of alcohols can be represented as:

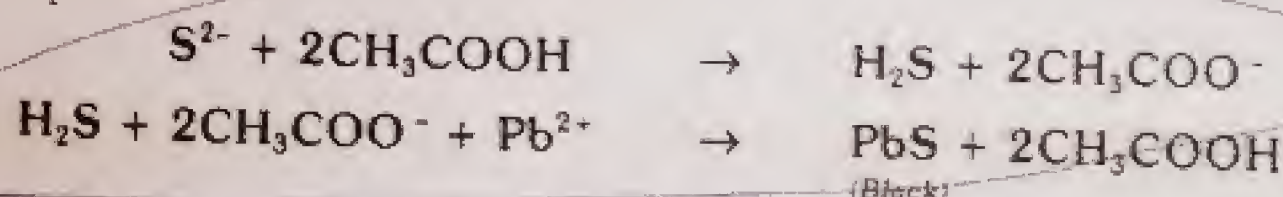
n	R	Formula
1	$\text{CH}_3-$	$\text{CH}_3\text{OH}$
2	$\text{CH}_3\text{CH}_2-$	$\text{CH}_3\text{CH}_2\text{OH}$

(vii) **How sulphur can be detected in organic compounds?**

Lassaigne's filtrate is prepared and acidified with acetic acid.

- The solution is boiled to expel  $\text{H}_2\text{S}$  gas.
- The  $\text{H}_2\text{S}$  gas turns lead acetate paper black that indicates the presence of Sulphur in the compound.

Reactions



**Q3: Give detailed answers for the following questions.**

(i) **What are the main sources of organic compounds?**

See Page 110

(ii) **Write down the characteristics of organic compound from inorganic compounds.**

See Page 113

(iii) **How organic compounds are used in our daily life?**

See Page 113

(iv) **Write down any ten functional groups of organic compounds? Give reasons for their importance of organic chemistry.**

See Page 116

(v) **Give the chemical tests for the detection of elements in organic compounds.**

See Page 119







b.	What happens if silver nitrate solution is added to the solution of chloride ions?	02
(ix)	What are fossil fuel? Give examples.	03
(x)	How bromine and nitrogen can be detected in an organic compound?	03
(xi) a.	Write down the structural formulae of (i) Naphthalene (ii) Anthracene	02
b.	Why organic compounds are insoluble in water?	01
(xii) a.	Name four drugs obtained from plants?	02
b.	Define destructive distillation?	01
(xiii) a.	How oxygen can be detected in organic compounds?	03
(xiv) a.	What is the importance of functional group.	02
b.	List different sources of organic compounds?	01
(xv) a.	Define fermentation.	01
b.	Differentiate between total and partial synthesis.	02
(xvi)	What is a rubefacient? Name two such compounds.	03
(xvii) a.	What are alkaloids?	02
b.	Why organic compounds are poor conductor of electricity?	02
(xviii)	Give brief reasons	
a.	What is coal?	01
b.	What we obtain by fractional distillation of coal gas?	01
c.	What is the simplest bucky ball?	01
(xix)	What are the general characteristics of homologous series?	03

### Section - C

**Note:** Attempt any TWO questions. All questions carry equal marks. (2 × 13 = 26)

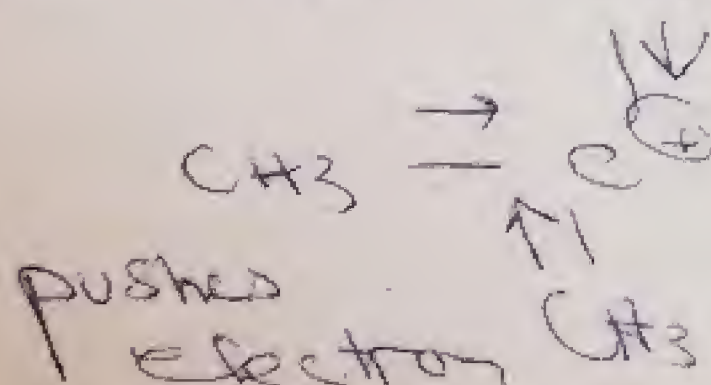
Q. 3.	a. Define organic compounds? Give their sources.	05
	b. Explain the chemistry of Lassaigne test?	05
	c. What are aliphatic and alicyclic compounds? Give examples and explain.	04
Q. 4.	a. Define functional groups? Give common functional groups found in organic compounds.	05
	b. Provide a brief review of importance of organic compounds.	05
	c. Give names of compounds which are exception to the modern definition of chemistry. Also give reason.	03
Q. 5.	a. Differentiate between organic and inorganic compounds with examples.	03
	b. How carbon can be detected in organic compounds?	04
	c. Give test for the detection of metals in organic compounds.	03
	d. What important products are obtained from petroleum?	03

\* Alkyl Groups are electron donating.

\* Tertiary alcohol are more reactive.

→ The alcohol, whose carbon cation is stable, is more reactive.

\* Tertiary carbon atom  $\text{CH}_3$





Hydrocarbons

## CHAPTER # 16

# HYDROCARBONS

Definition:

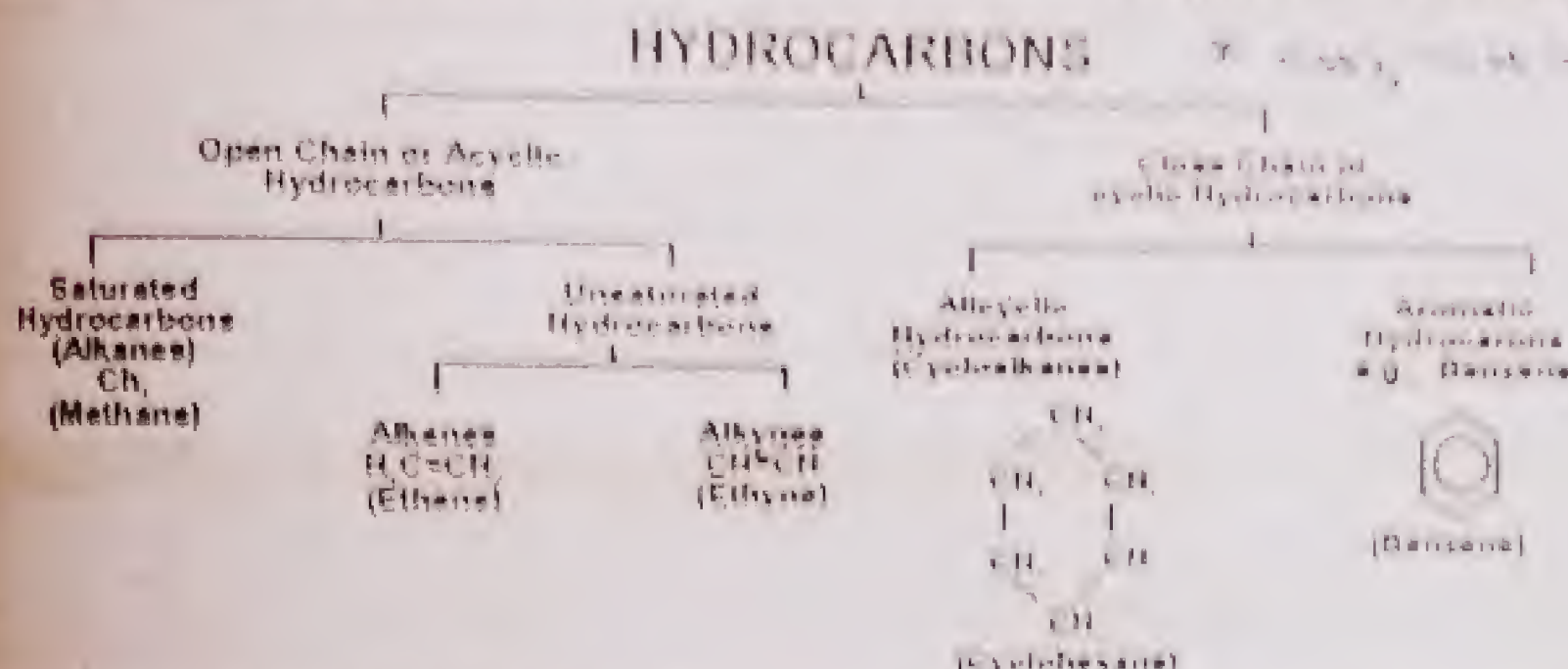
The ability of carbon atoms to attach with each other to form a chain or ring is called **catenation**. Thus carbon has the ability to form long chains, multiple bonds and rings.

Hydrocarbons:

Organic compounds which contain carbon and hydrogen only are called hydrocarbons.

## TYPES OF HYDROCARBONS

The hydrocarbons have been divided into various classes on the basis of their structure as given below.



## OPEN CHAIN HYDROCARBONS

The hydrocarbons, in which carbon atoms attached with each other to form open chains are called open chain hydrocarbons.

### TYPES OF OPEN CHAIN HYDROCARBONS:

These are of two types

- (1) Saturated hydrocarbons (Alkanes or Paraffins)
- (2) Unsaturated hydrocarbons (Alkenes or Olefins) and (Alkynes or Acetylenes)

### (1) SATURATED HYDROCARBONS

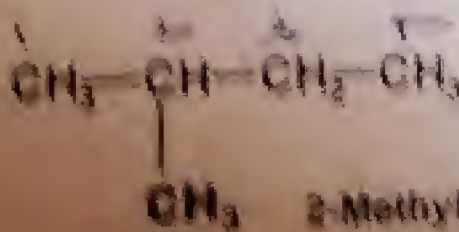
These are the hydrocarbons in which carbon atoms are attached with each other through single bonds.

- Each carbon atom is  $sp^3$  hybridized, e.g. Alkanes
- These may have straight chain or branched chain
- No further atoms or groups of atoms can be attached to the carbon atoms of such hydrocarbons. That is why they are called saturated hydrocarbons.

Examples:



n-Pentane (a straight chain alkane)



2-Methylbutane (a branched chain alkane)



## (2) UNSATURATED HYDROCARBONS

These are the hydrocarbons in which at least two carbon atoms are attached through double or triple bonds and are  $sp^2$  or  $sp$  hybridized, e.g., alkenes and alkynes.

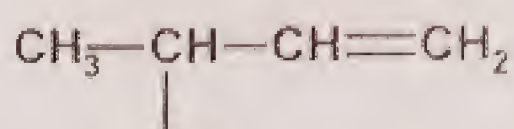
### (i) Alkenes or Olefins:

These are the unsaturated hydrocarbons in which at least two carbon atoms are  $sp^2$  hybridized and form a double bond with each other.

- Alkenes may be straight chain or branched chain.



1-Pentene (a straight chain alkene)



2-Methyl-1-butene (a branched chain alkene)

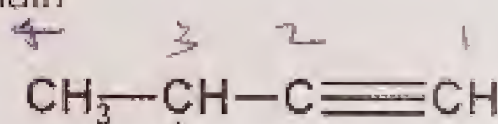
### (ii) Alkynes or Acetylenes:

These are the unsaturated hydrocarbons in which at least two carbon atoms are  $sp$  hybridized and form a triple bond with each other.

- Alkynes may be straight chain or branched chain



1-Pentyne (a straight chain alkyne)



2-Methyl-1-butyne (a branched chain alkyne)

## CLOSED CHAIN HYDROCARBONS:

These are the hydrocarbons in which carbon atoms attach with each other to form rings.

### TYPES OF CLOSED CHAIN HYDROCARBONS:

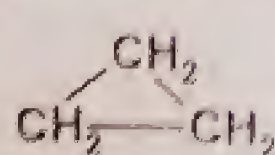
These are of two types.

- Alicyclic Hydrocarbons.
- Aromatic Hydrocarbons.

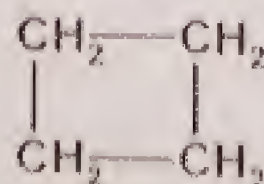
#### (1) ALICYCLIC HYDROCARBONS:

Non-benzenoid cyclic hydrocarbons are alicyclic hydrocarbons.

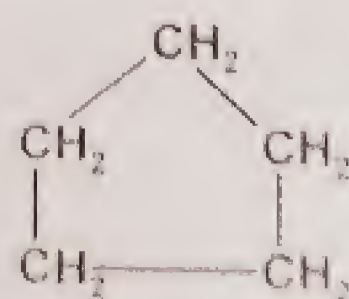
Alicyclic hydrocarbons possess two hydrogen atoms less than their corresponding open chain hydrocarbons



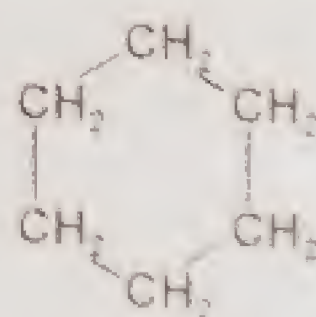
Cyclopropane



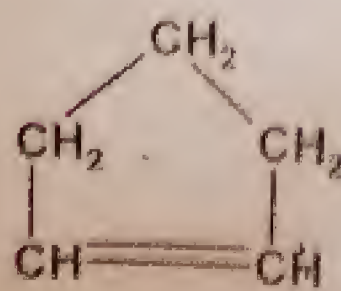
Cyclobutane



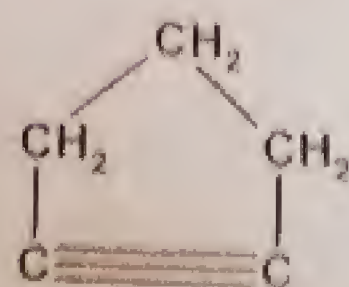
Cyclopentane



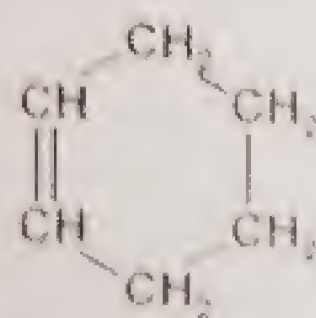
Cyclohexane



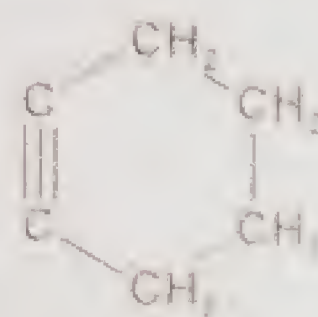
Cyclopentene



Cyclopentyne



Cyclohexene



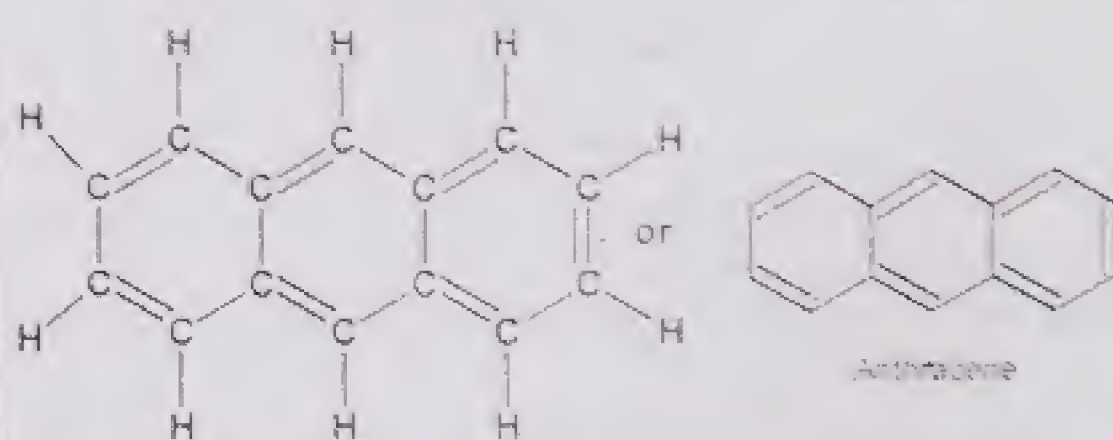
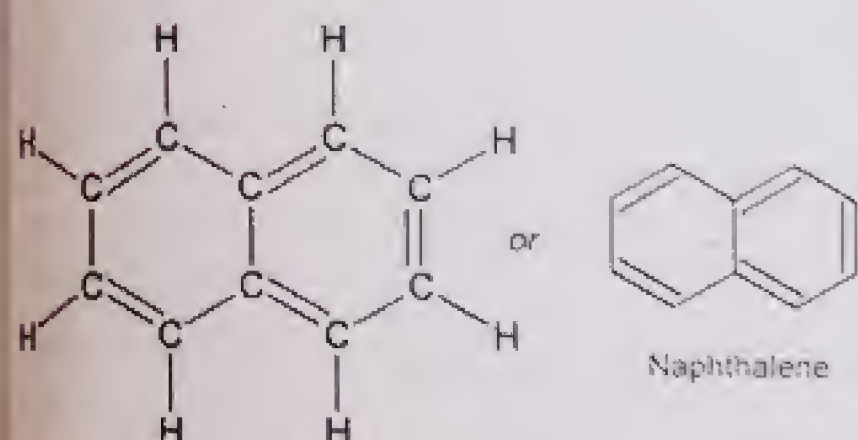
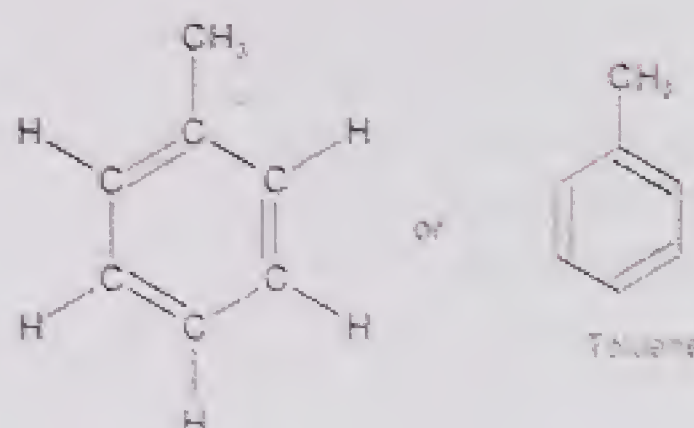
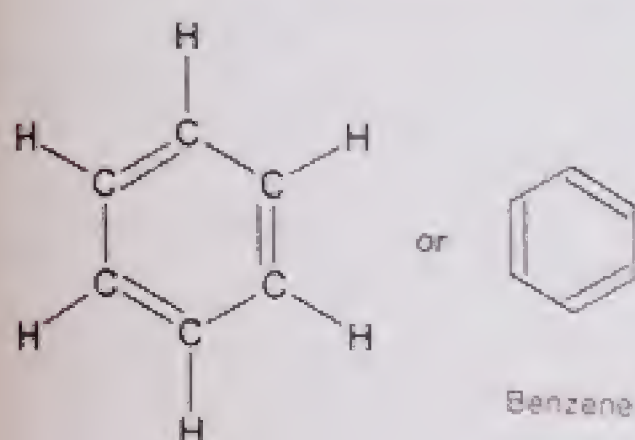
Cyclohexyne



## AROMATIC HYDROCARBONS:

**Benzenoid cyclic hydrocarbons** are known as **aromatic hydrocarbons**.

- In these compounds all the carbon atoms present in the ring are  $sp^2$ -hybridised.
- Benzene is the simplest aromatic hydrocarbon. It has a regular hexagonal structure with alternate single and double bonds between carbon atoms.



## QUICK QUIZ-1

1) What is catenation?

The ability of carbon atoms to attach with each other to form a chain or ring is called Catenation. Thus carbon has the ability to form long chains, multiple bonds and rings.

e.g.  $H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$  (n-Octane)

2) What are hydrocarbons?

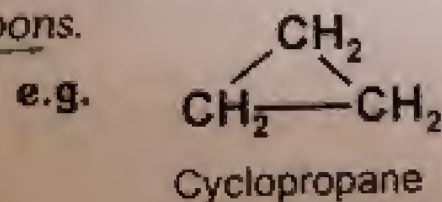
Organic compounds which contain carbon and hydrogen only are called hydrocarbons.

These are of mainly two types.

- The hydrocarbons, in which carbon atoms attached with each other to form open chains are called open chain hydrocarbons.

e.g.  $H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$  (n-Octane)

- The hydrocarbons in which carbon atoms attach with each other to form rings are called closed chain hydrocarbons.



3) Why **saturated hydrocarbons** are called **paraffins**

Aliphatic saturated hydrocarbons called alkanes are highly unreactive. Hence these are also called Paraffins (Latin: Parum = little + affins = affinity). It means little reactivity.

The unreactivity of alkanes is due to the inertness of a  $\sigma$ -bond and non-polar C-H, C-C bonds.

**Examples:** Methane, ethane etc.



Having carbon atoms which are linked in open chain, hydrocarbon which do not contain a benzene ring is called aliphatic carbon.

(4) Why unsaturated hydrocarbons are called olefins

Aliphatic unsaturated hydrocarbons having double bond are called Alkenes. These are also called Olefins (Latin: *oleum*=oil + *facere*=to make). It means oil forming substances. This term is used because lower members of this class, e.g. ethene form oily liquids on reaction with  $\text{Cl}_2$  gas.

(5) What is hybridization

The process in which atomic orbitals of different energy and shape are mixed together to form a new set of equivalent orbitals of same energy and same shape is called hybridization.

- The new orbitals formed are called hybrid orbitals.
- The concept of hybridization is used to explain number of valence, equivalent valence, bond angles etc. of covalent molecules.
- There are various types of hybridization depending upon the number and nature of orbitals taking part in hybridization, e.g.,  $\text{sp}^3$ ,  $\text{sp}^2$ ,  $\text{sp}$ ,  $\text{dsp}^2$ ,  $\text{dsp}^3$ ,  $\text{d}^2\text{sp}^3$  etc.

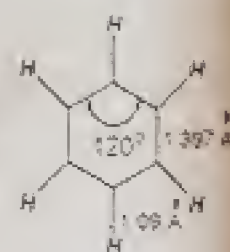
(6) Why benzene is called aromatic hydrocarbons

- The term aromatic is derived from Greek word 'aroma' meaning 'fragrant'.
- Initially this term was used for such compounds which contain low hydrogen to carbon ratio, shows high chemical stability and have characteristic smell. However, later on, many stable compounds of this type were found odourless. Thus term 'aromatic' became associated with chemical stability of compound instead of odour.
- Since, benzene has low hydrogen to carbon ratio and shows high chemical stability, so it is called aromatic hydrocarbon.

(7) What is hexagonal structure?

A regular hexagonal structure has six equal faces and all angles of  $120^\circ$ .

e.g. benzene has hexagonal planar structure in which all carbon and hydrogen atoms are present in the same plane. All the angles are of  $120^\circ$ . All C - C bond lengths are equal (1.397 Å). Similarly all C - H bond lengths are also equal (1.09 Å).



## ALKANES AND CYCLOALKANES

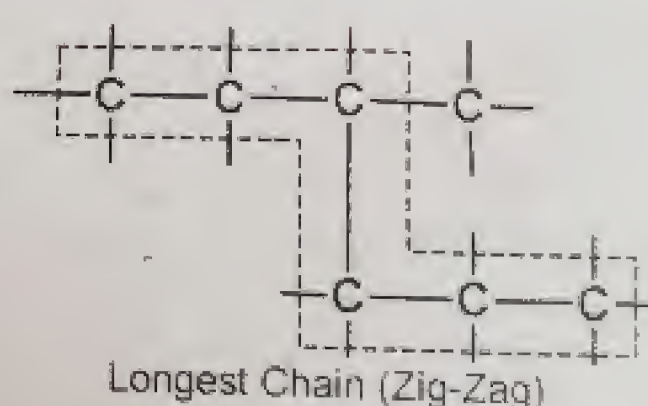
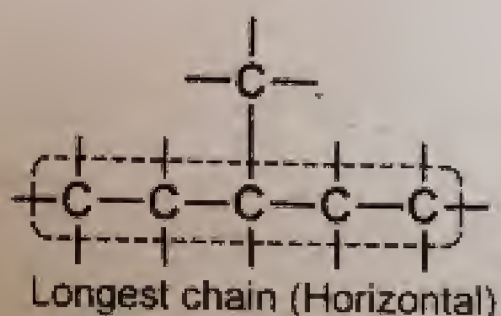
### ALKANES

Acyclic saturated hydrocarbons are called alkanes.

- These are simplest organic molecules with only C and H atoms.
- Their general formula is  $\text{C}_n\text{H}_{2n+2}$
- These are commercially important as fuels and oils.

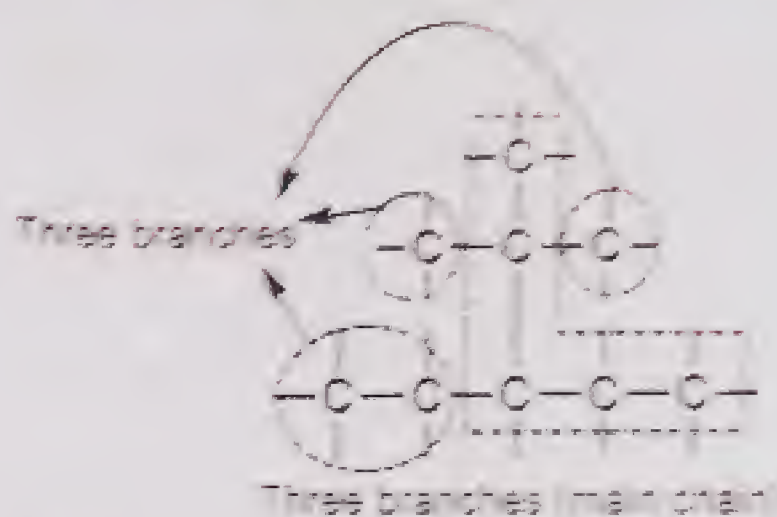
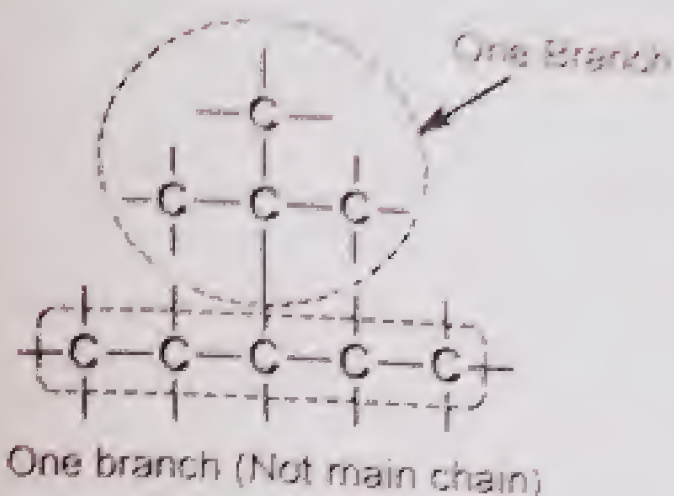
### I.U.P.A.C. NOMENCLATURE OF ALKANES:

- Locate the largest continuous chain of carbon atoms independent of direction of the chain. It is called main chain, stem, principal chain or parent chain.

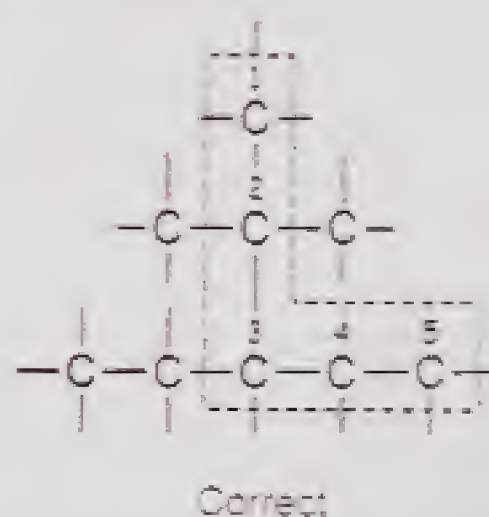
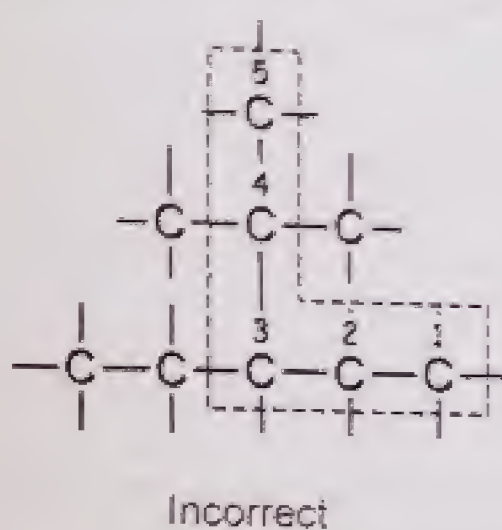




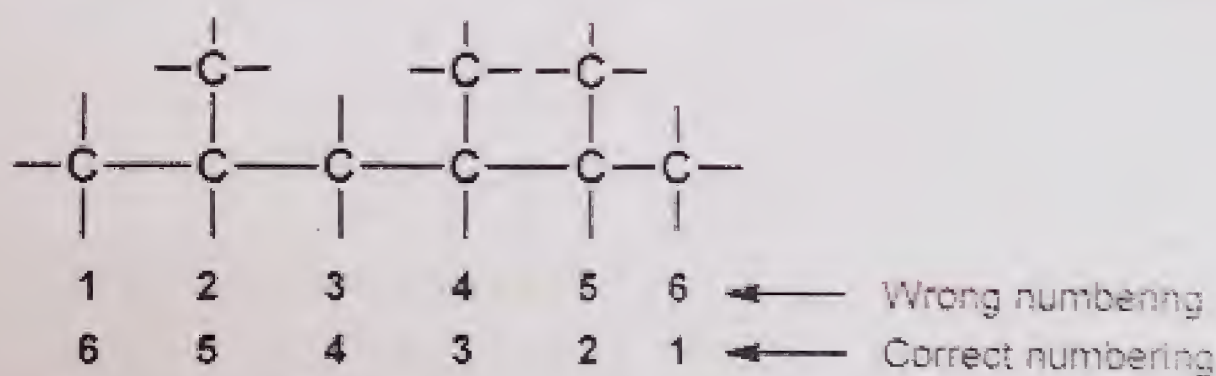
- (2) If there are two or more chains of equal length, the chain with larger number of branches is selected as main chain.



- (3) Number the main chain starting from the end nearest to the substituent.

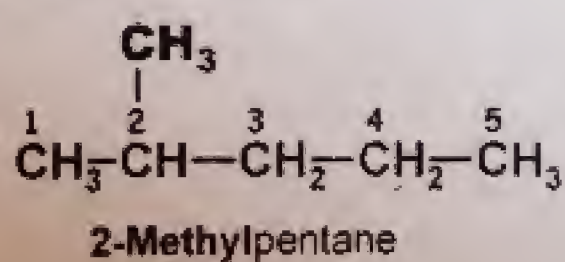


- (4) When two identical substituents are present at equal distance from either end, number the chain starting with end which gives their minimum sum.

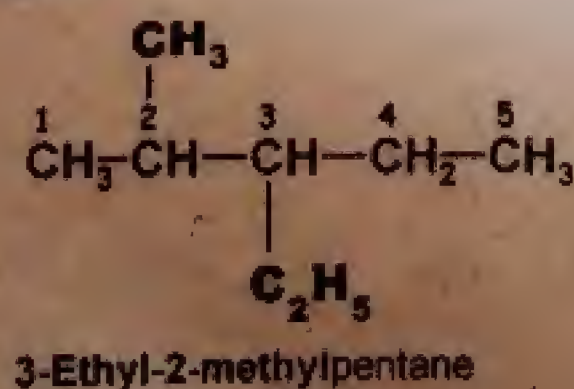


Since the sum of number  $2+3+5=10$ , is less than  $2+4+5=11$ , the correct numbering starts from the right.

- (5) The position of substituent is indicated by the number of C-atom to which it is attached. The number is prefixed to the name of group separated by hyphen.

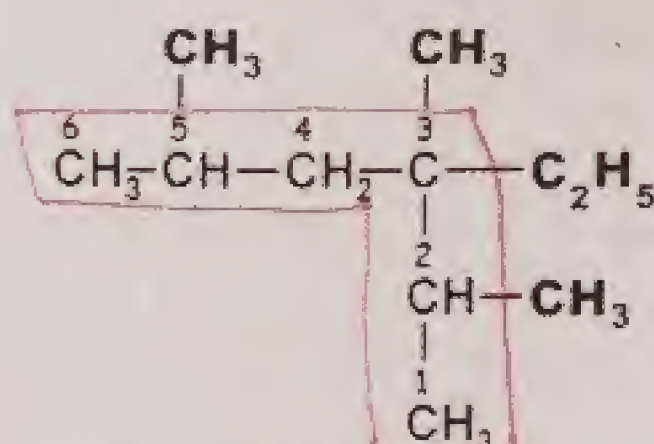


- (6) Names of alkyl groups are written before the name of parent hydrocarbon in alphabetical order or in order of increasing size, separated by hyphen.



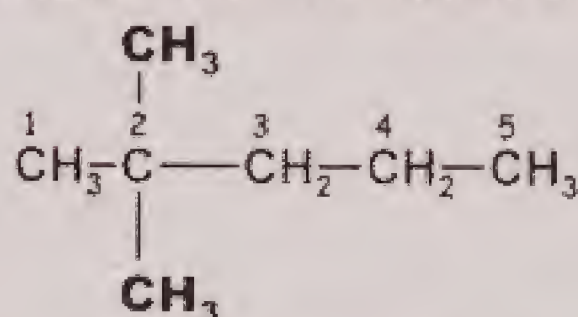


- (7) When two or more like groups are present, their numbers are indicated by prefixes di, tri-, tetra-, etc. Their numbers are grouped together and are separated by commas.



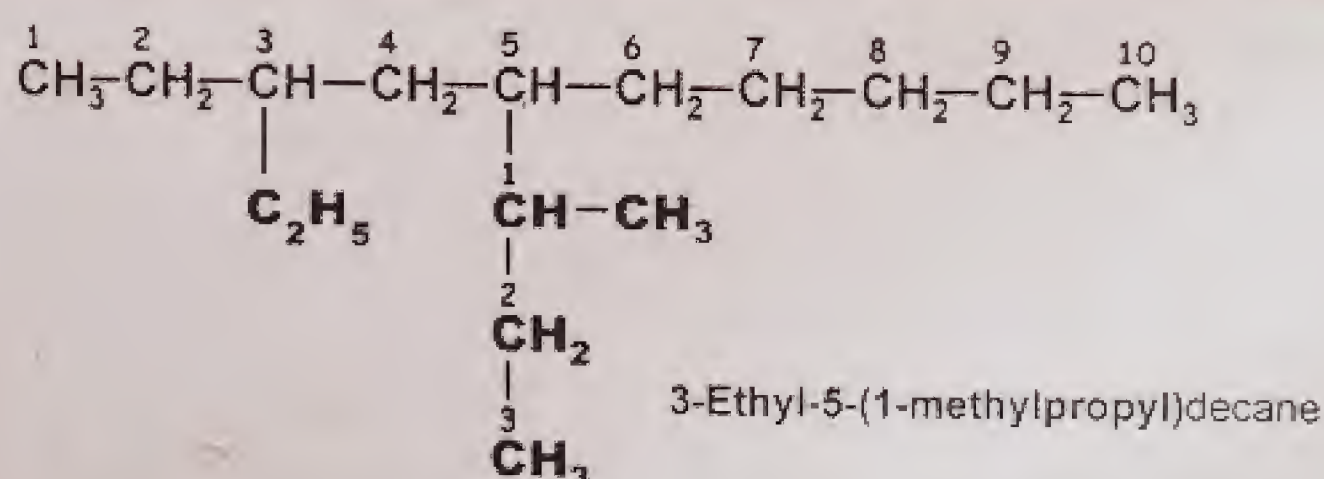
3-Ethyl-2,3,5-trimethylhexane

- (8) If two identical groups appear at the same c-atom, the number is separated twice, separated by commas.



2,2-Dimethylpentane

- (9) The longest chain of the substituent is numbered starting with the carbon attached directly to the main chain. Parentheses are used to separate the numbering of the substituent and the main chain.



3-Ethyl-5-(1-methylpropyl)decane

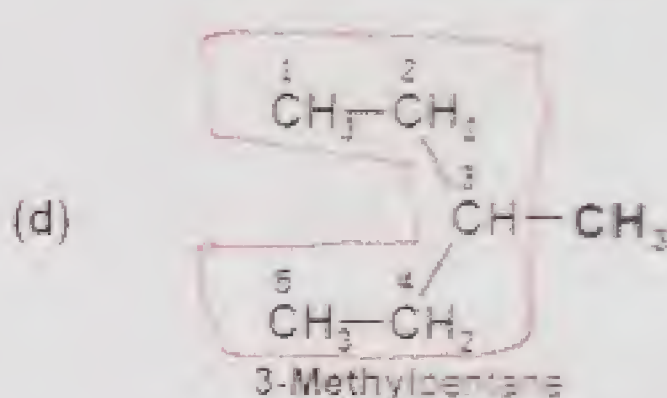
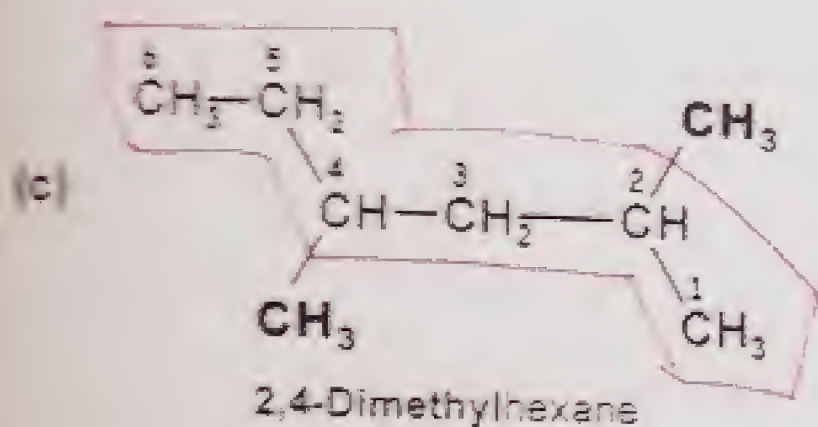
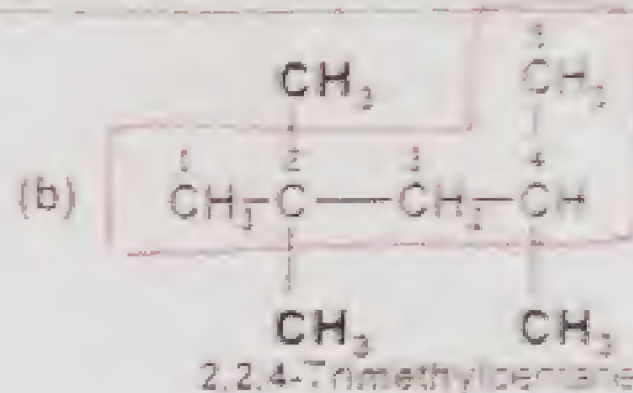
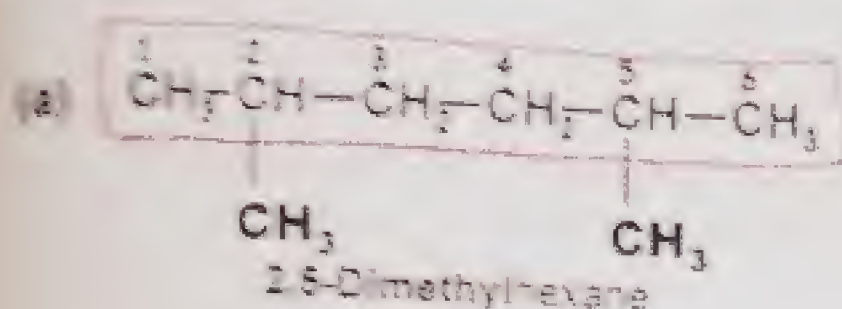
The structural formula and names for the simple alkanes are shown in the following table.

Number of Carbon atoms	Formula	Line drawing	Alkane Name
1	CH <sub>4</sub> or	Not applicable (N/A)	Methane
2	C <sub>2</sub> H <sub>6</sub> or CH <sub>3</sub> - CH <sub>3</sub>		Ethane
3	C <sub>3</sub> H <sub>8</sub> or CH <sub>3</sub> - CH <sub>2</sub> - CH <sub>3</sub>		Propane
4	C <sub>4</sub> H <sub>10</sub> or CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>2</sub> - CH <sub>3</sub>		Butane
5	C <sub>5</sub> H <sub>12</sub> or CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>3</sub> - CH <sub>3</sub>		Pentane
6	C <sub>6</sub> H <sub>14</sub> or CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>4</sub> - CH <sub>3</sub>		Hexane
7	C <sub>7</sub> H <sub>16</sub> or CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>5</sub> - CH <sub>3</sub>		Heptane
8	C <sub>8</sub> H <sub>18</sub> or CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>6</sub> - CH <sub>3</sub>		Octane
9	C <sub>9</sub> H <sub>20</sub> or CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>7</sub> - CH <sub>3</sub>		Nonane
10	C <sub>10</sub> H <sub>22</sub> or CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>8</sub> - CH <sub>3</sub>		Decane



# ACTIVITY

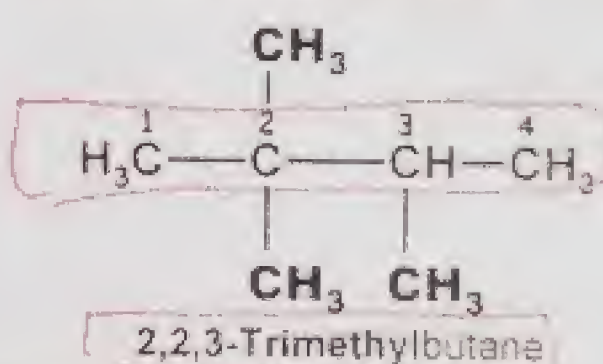
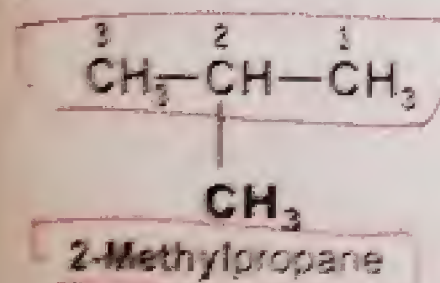
Name each of the following compounds according to IUPAC System.



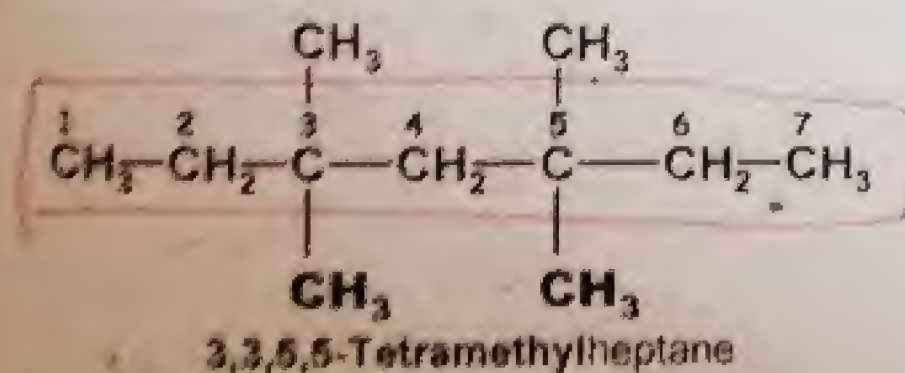
Indicate what is wrong with each of the following names. Give the correct IUPAC names if possible.

(a) 2-Dimethyl Propane

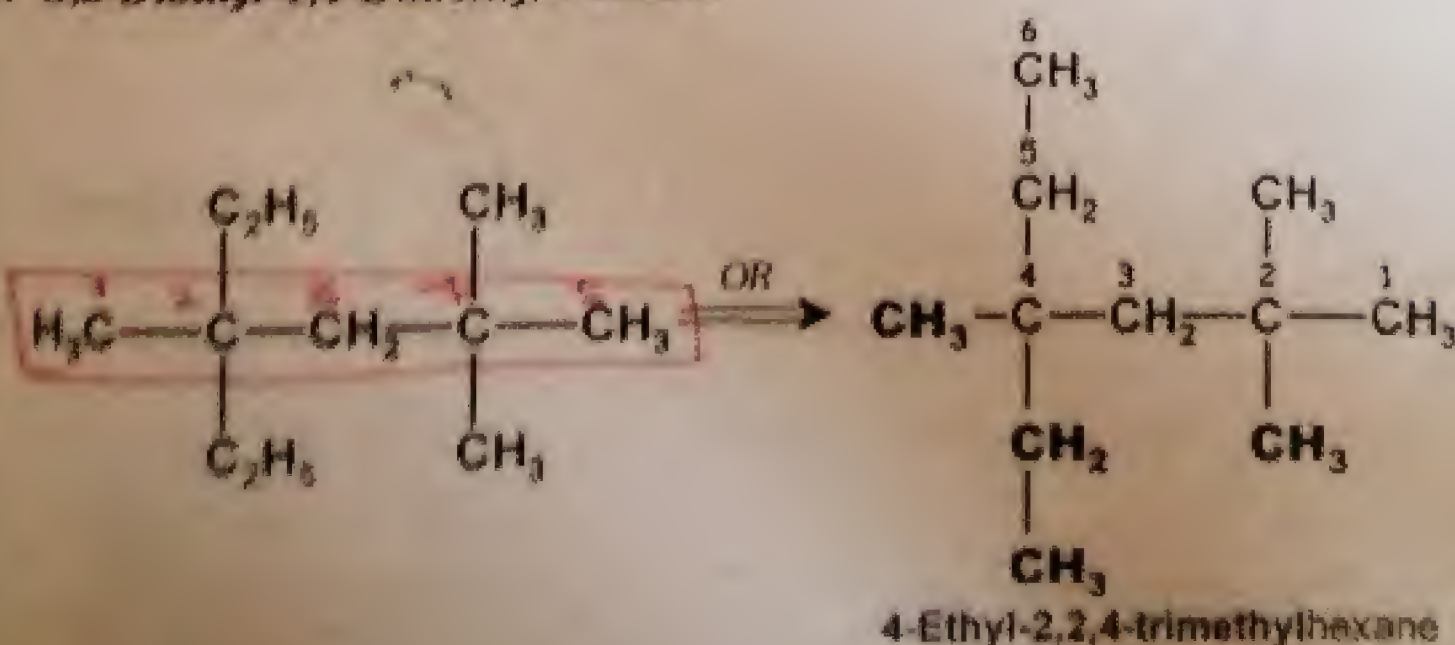
(b) 2,2,3-Methyl Butane



(c) 3,3-Dimethyl-5,5-Dimethyl Heptane

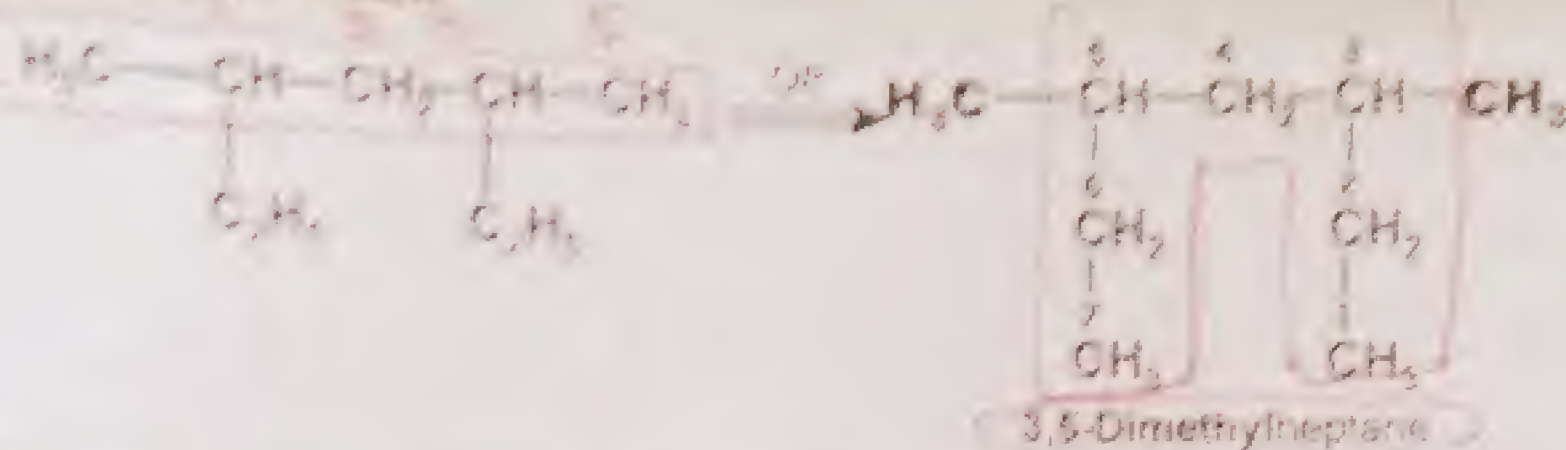


(d) 2,2-Diethyl-4,4-Dimethyl Pentane

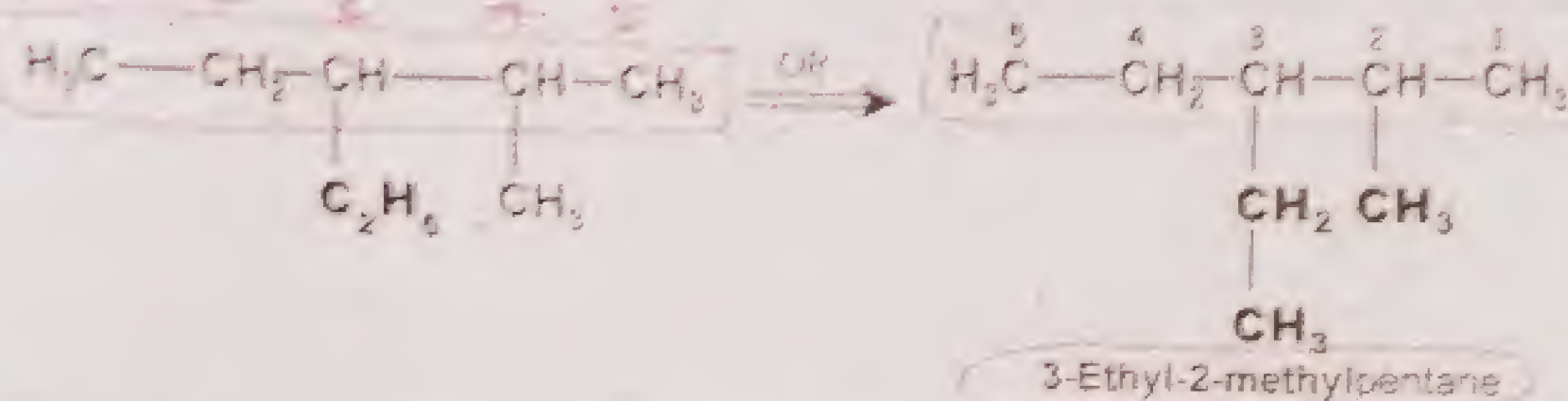




(a) 2,4-Dimethyl Pentane

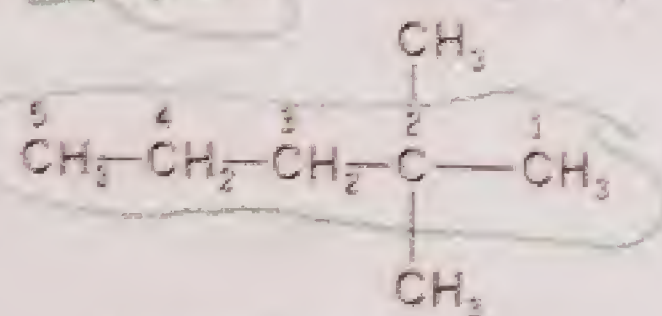


(b) 3-Ethyl-2-Methyl Pentane

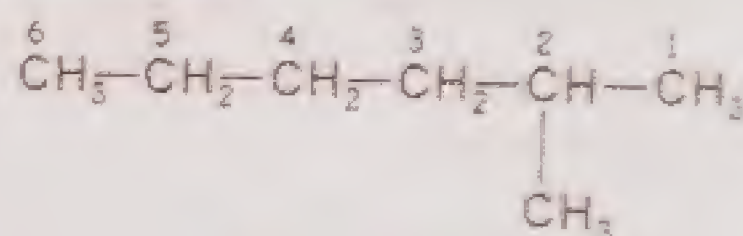


3. Write the structures of the following compounds.

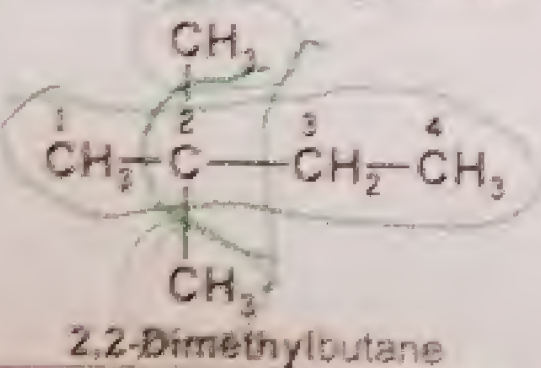
(a) Neohexane



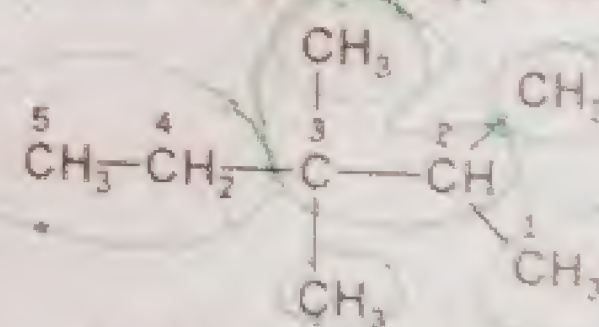
(b) Isoheptane



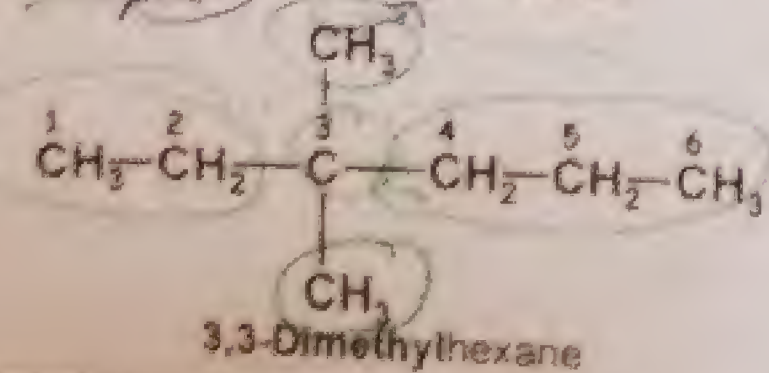
(c) Trimethyl Ethyl Methane



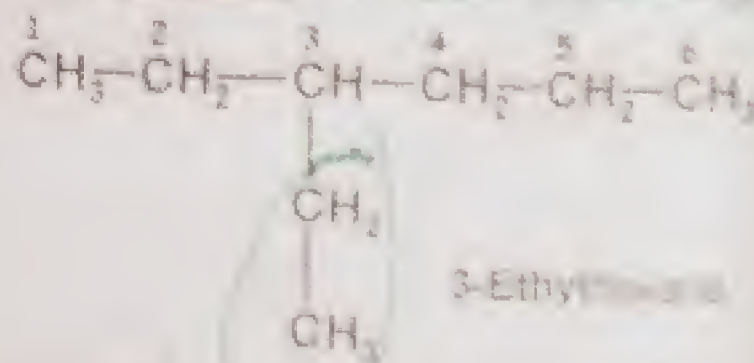
(d) Dimethyl Ethyl Isopropyl Methane



(e) Dimethyl Propyl Ethyl Methane



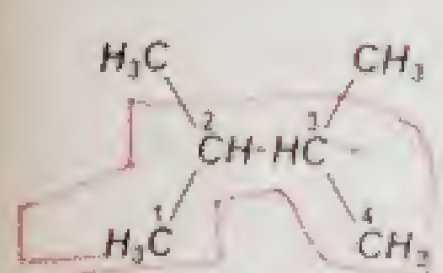
(f) 3-Ethylhexane



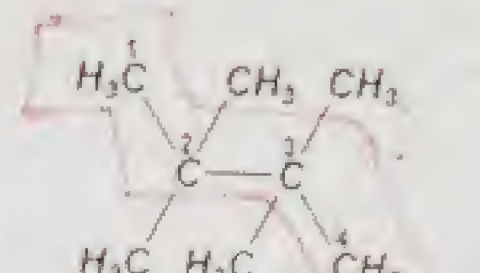


**MORE PRACTICE**

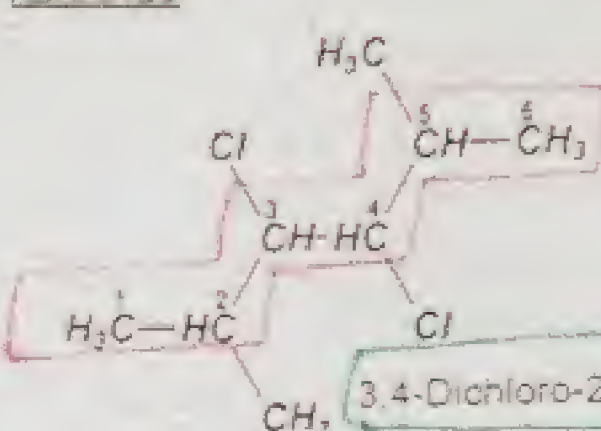
ALKANES



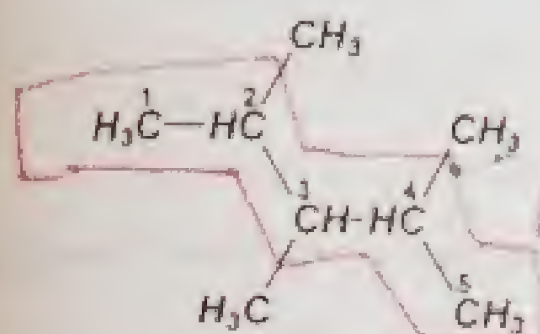
2,3-Dimethylbutane



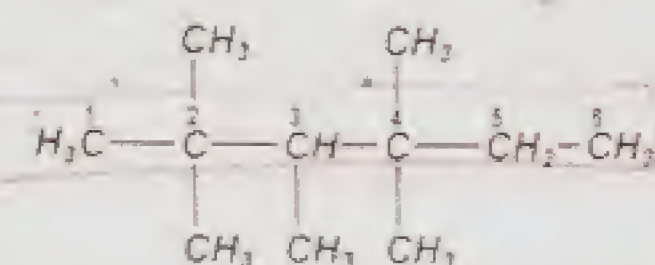
2,2,3,3-Tetramethylbutane



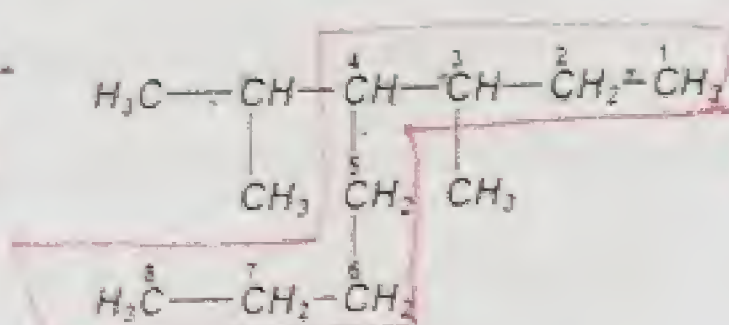
3,4-Dichloro-2,5-dimethylhexane



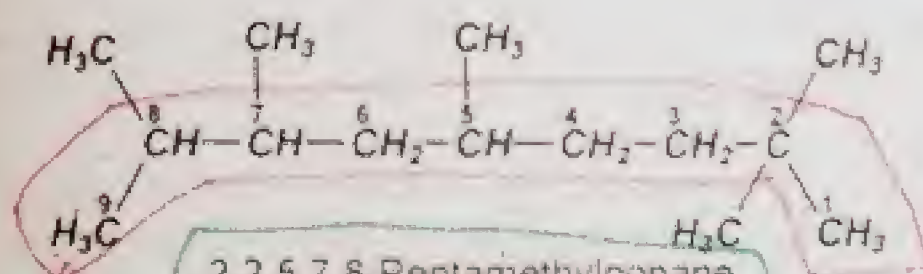
2,3,4-Trimethylpentane



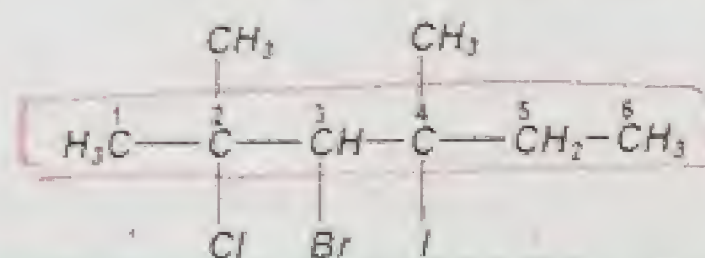
2,2,3,4,4-Pentamethylhexane



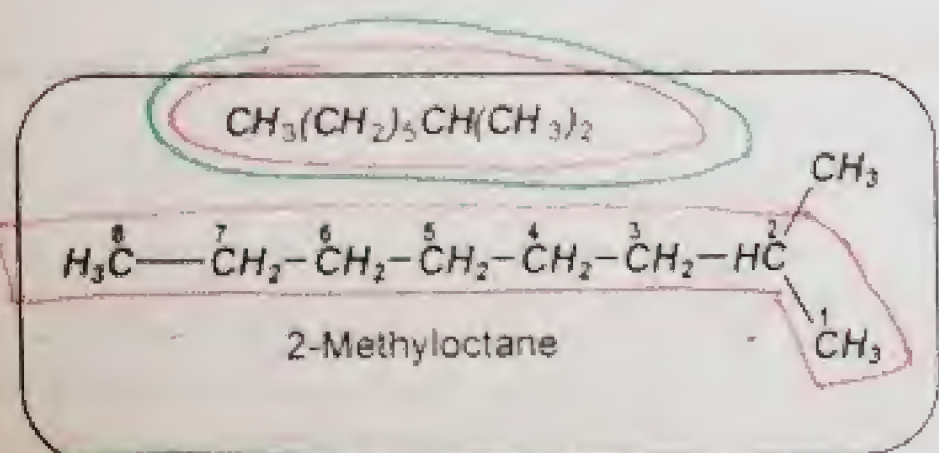
4-iso-Propyl-3-methyloctane



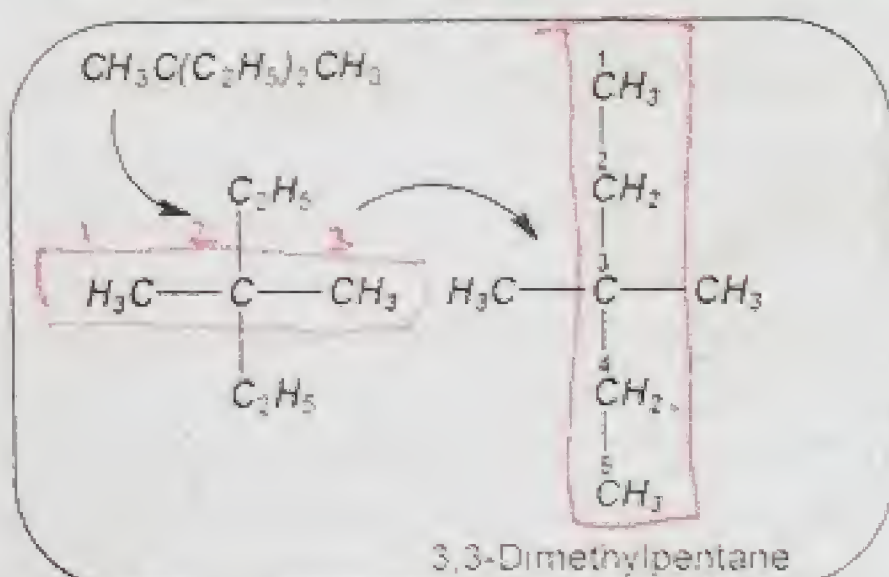
2,2,5,7,8-Pentamethylnonane



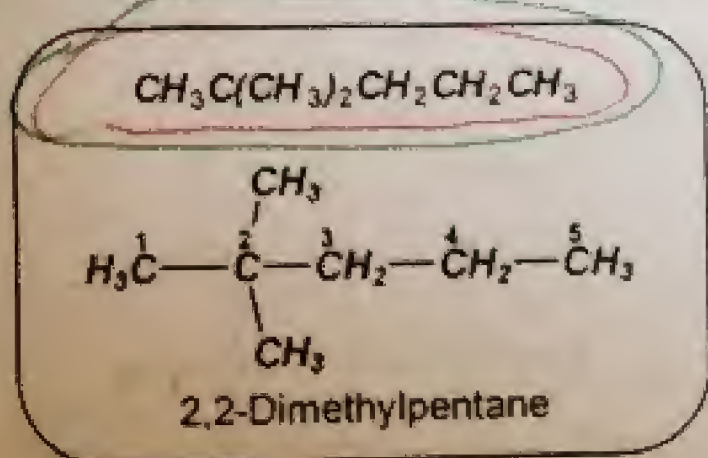
3-Bromo-2-chloro-4-iodo-2,4-dimethylhexane



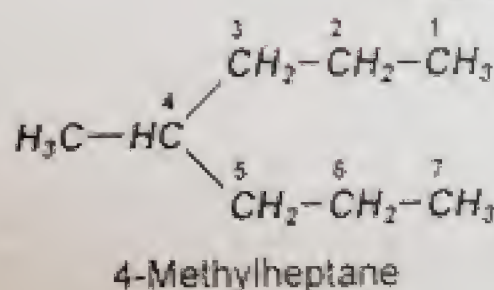
2-Methyloctane



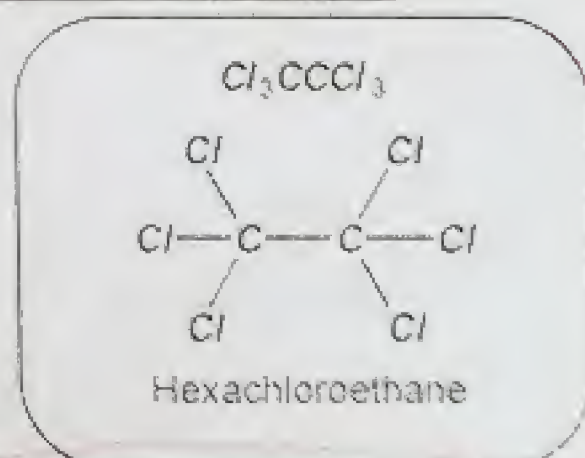
3,3-Dimethylpentane



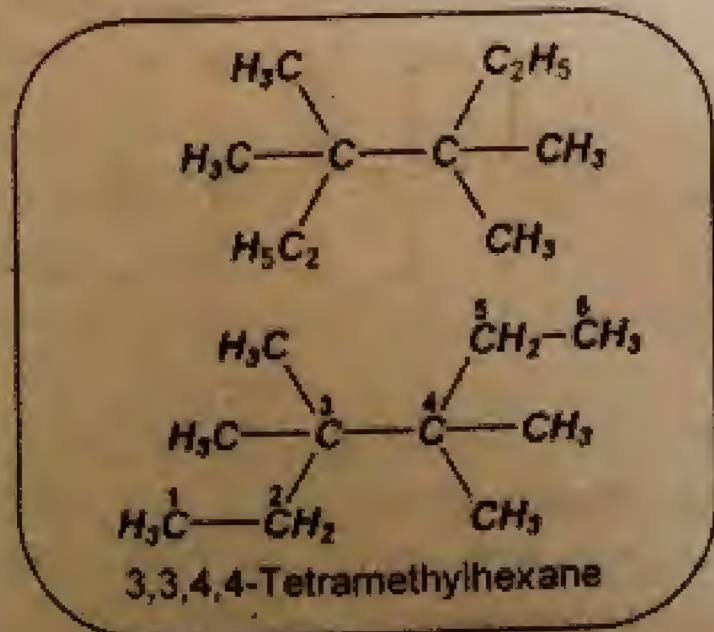
2,2-Dimethylpentane



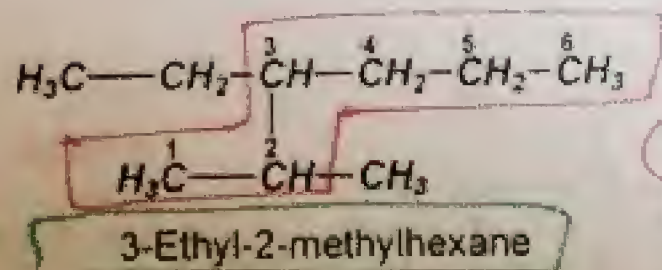
4-Methylheptane



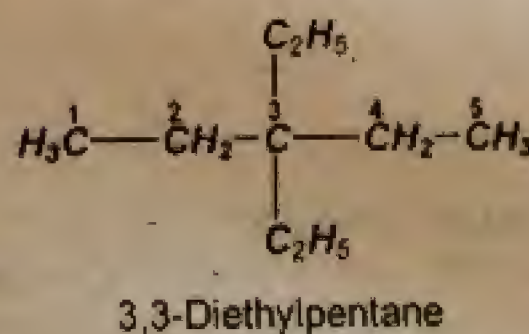
Hexachloroethane



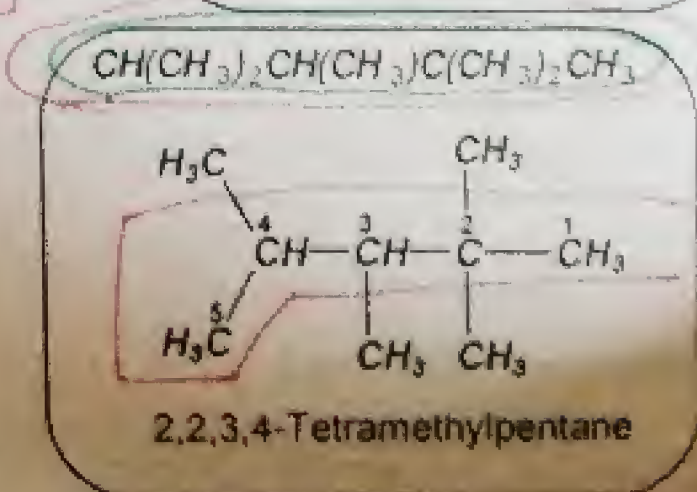
3,3,4,4-Tetramethylhexane



3-Ethyl-2-methylhexane



3,3-Diethylpentane



2,2,3,4-Tetramethylpentane



## PHYSICAL PROPERTIES

- (1) Methane to Butane are colorless, odorless gases. Pentane to heptadecane are liquids. The higher members from  $C_{18}$  onwards are waxy solids which are also odorless and tasteless.
- (2) Alkanes are non-polar or very weakly polar. These are insoluble in polar solvents like water but soluble in non-polar solvents like benzene, ether, carbon tetrachloride, etc.
- (3) Their boiling points, melting points, density etc. increase with the increase in number of carbon atoms, whereas solubility decreases with the increase in mass.
- (4) The boiling points increase by  $20$  to  $30^\circ\text{C}$  for addition of each  $\text{CH}_2$  group to the molecule.
- (5) The boiling points of straight chain alkanes are higher than their isomeric branched chain alkanes.  
e.g. n-butane has a higher boiling point ( $-0.4^\circ\text{C}$ ) than isobutane ( $-11.2^\circ\text{C}$ ).

### QUICK NOTE:

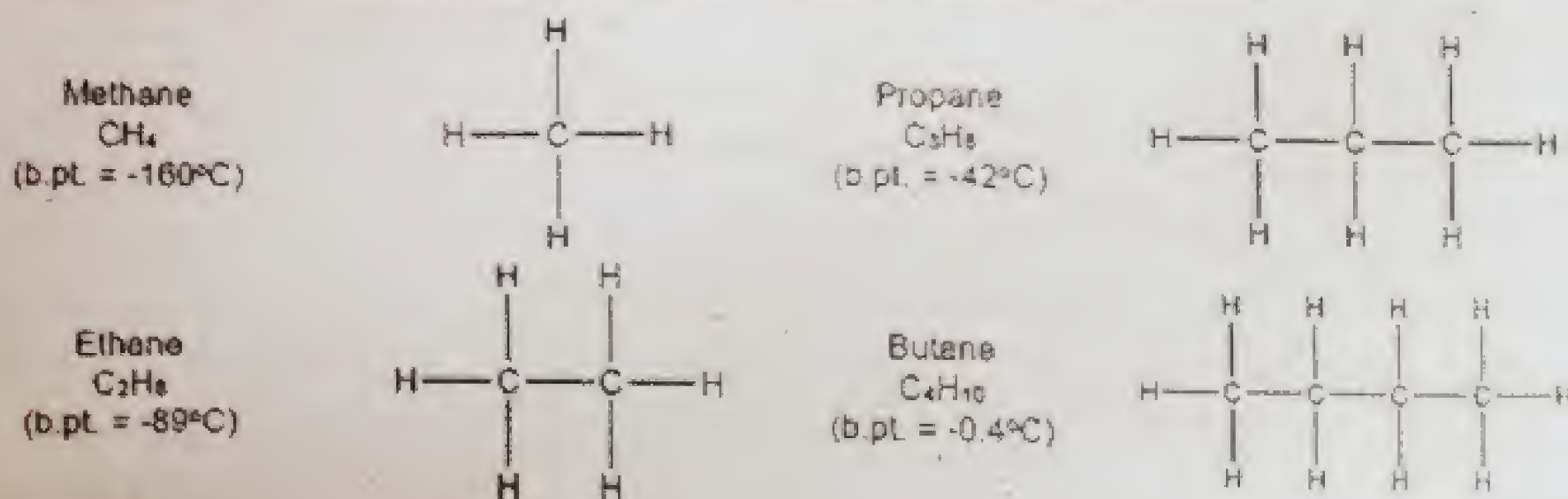
**Effect of branching on melting point of alkanes.** Generally, branched molecules (being spherical) have less surface area than linear molecules. The linear alkanes have higher melting point than branched alkanes. It is because linear molecules have more surface area and more contact with other molecules. So, these are difficult to separate and melting point is higher. e.g. the m.p. of n-pentane is higher than iso-pentane. However, when molecules become highly branched they become more spherical and their surface area is highly reduced. So, the molecules become tightly packed in solid state and less energy is required to separate them. Hence, melting point increases. e.g. melting point of neo-pentane is higher than n-pentane and iso-pentane.

**Effect of branching on boiling point of alkanes.** Generally, branched molecules (being spherical) have less surface area than linear molecules. Thus, in liquid state sphere-type molecules are easier to separate while linear molecules are tangled with each other (like noodles) and have more contact with other molecules. So, they have stronger forces and are difficult to separate. Hence boiling point decreases with increase in branching. e.g. the order of b.p. in pentanes is n-pentane > iso-pentane > neo-pentane.

## STRUCTURE

### Normal Alkanes:

- Alkanes are the simplest organic compounds consisting of only  $sp^3$  hybridized C and H atoms connected by  $\sigma$ -bonds.
- They have a generic formula of  $\text{C}_n\text{H}_{2n+2}$ . This formula also defines the maximum number of hydrogen atoms present for a given number of C atoms.
- Structures of the simple  $\text{C}_1$  to  $\text{C}_4$  alkanes are shown below in a variety of representations.
- As the number of C atoms increases then other isomeric structures are possible.



### Isomeric Alkanes:

- The molecular formula for the  $\text{C}_1$  to  $\text{C}_3$  alkanes lead to single, unique structures.
- However for  $\text{C}_4\text{H}_{10}$ , there are two possible constitutional isomers.
- The isomers have different chemical, physical properties and biological properties.



ALKANE: SOME IMPORTANT PHYSICAL PROPERTIES

<b>n-Butane</b>	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$	$t_b = -0.5^\circ\text{C}$ $t_m = -138.4^\circ\text{C}$ $\Delta H_f = -125.6 \text{ kJ/mol}$ (-30.0 kcal/mol) $\Delta H_c = -2877 \text{ kJ/mol}$ (-687 kcal/mol)
<b>Isobutane</b>	$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	$t_b = -10.8^\circ\text{C}$ $t_m = -93.8^\circ\text{C}$ $\Delta H_f = -135.5 \text{ kJ/mol}$ (-32.4 kcal/mol) $\Delta H_c = -2866 \text{ kJ/mol}$ (-685 kcal/mol)

ALKANE: SOME IMPORTANT PHYSICAL PROPERTIES

<b>n-Pentane</b>	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	$t_b = 36.1^\circ\text{C}$ $t_m = -129.7^\circ\text{C}$ $\Delta H_f = -120.9 \text{ kJ/mol}$ (-28.9 kcal/mol)
<b>Isopentane</b>	$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	$t_b = 27.8^\circ\text{C}$ $t_m = -95.1^\circ\text{C}$ $\Delta H_f = -115.1 \text{ kJ/mol}$ (-27.5 kcal/mol)
<b>Neopentane</b>	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	$t_b = 9.5^\circ\text{C}$ $t_m = -15.9^\circ\text{C}$ $\Delta H_f = -103.6 \text{ kJ/mol}$ (-24.7 kcal/mol)

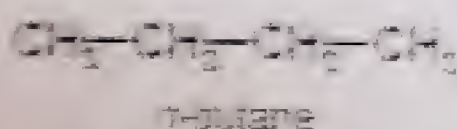
Definition

Alkane is a saturated hydrocarbon with a methyl group at second last carbon atom is termed as "Ethyl" and the methyl group at second last carbon atom is termed as "Neo".

Alkyl Radical

Alkyl radical is a group of atoms that is less stable.

eg. 1-methylpropane is more stable than 1-butane.



Alkanes

Alkanes are saturated hydrocarbons. Hence they are also called Paraffin.

Alkyl Radical is a group of atoms that is less stable. Unsaturation of Alkanes due to two factors

The Alkanes and Paraffins are most common stable alkyls, oxidizing and reducing agents under normal conditions.

Properties

Alkanes are saturated hydrocarbons. They are stable in the form of a  $\sigma$ -bond and non-polar C-H/C-C bonds.

Structure of Alkanes

Alkanes are saturated hydrocarbons. They are stable in the form of a  $\sigma$ -bond and non-polar C-H/C-C bonds.

Alkanes are saturated hydrocarbons. They are stable in the form of a  $\sigma$ -bond and non-polar C-H/C-C bonds.



### (iii) Non-polar Bonds:

- The electronegativity of carbon (2.5) and hydrogen (2.1) do not differ appreciably. Therefore, the bonding electrons between C-H and C-C are equally shared and bonds become non-polar. Hence, the ionic reagents such as acids, alkalis, oxidizing agents, etc. find no place in the alkane molecules for reaction.
- However, under suitable condition, Alkanes give two types of reactions:
  - Thermal and Catalytic Reactions
  - Substituted Reactions
- These reactions take place at high temperature or on absorption of light energy through the formation of highly reactive free radicals.

## CYCLOALKANES

Another type of molecule containing only  $sp^3$  hybridized C and H atoms, connected by  $\sigma$ -bonds is possible with a ring of 3 or more C atoms. These are the cycloalkanes. These are both synthetic and natural.

### NOMENCLATURE:

- According to IUPAC system, cycloalkanes with one ring are named by prefixing cyclo to the name of the corresponding alkane having the same number of carbon atoms as the ring.

Examples:



Cyclopropane



Cyclobutane

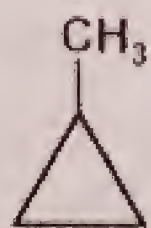


Cyclopentane

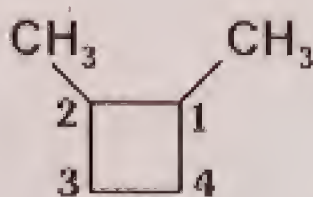


Cyclohexane

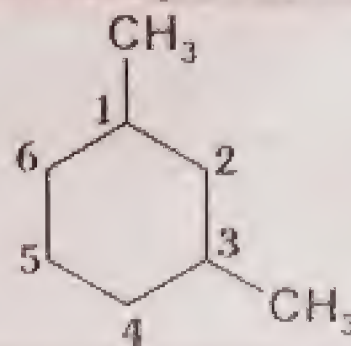
- The substituents are numbered in such a way that the sum of numbers is kept minimum, e.g.,



Methylcyclopropane



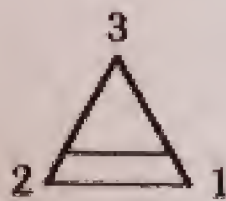
1,2-Dimethylcyclobutane



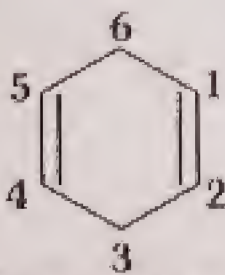
1,3-Dimethylcyclohexane

- If the alicyclic hydrocarbon is unsaturated, the rules applied to alkenes (for double bond) or alkynes (for triple bond) are used. Multiple bonds are given the lowest possible number.

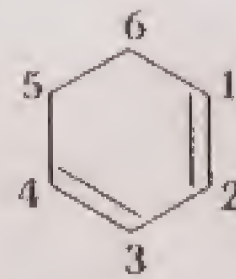
Examples:



Cyclopropene



Cyclohexa-1,4-diene



Cyclohexa-1,3-diene





### PHYSICAL PROPERTIES:

- Cycloalkanes have low polarity. Thus the only intermolecular forces between molecules of cycloalkanes are the very weak induced dipole - induced dipole forces, also known as London dispersion forces.
- These forces can be easily overcome. As a result, compared to other functional groups, but like alkanes, cycloalkanes tend to have low melting and boiling points.



**STRUCTURE:**

- They have a generic formula of  $C_nH_{2n}$ . Thus, these have two less H atoms than corresponding alkanes.
- These are isomers of alkenes.
- They have  $sp^3$ -hybridized carbon atoms.

Cyclopropane	$C_3H_6$	
Cyclobutane	$C_4H_8$	
Cyclopentane	$C_5H_{10}$	
Cyclohexane	$C_6H_{12}$	

**ACTIVITY:**

- The reactivity is very similar to the closely related alkanes which have the same types of bonds.
- Since C and H atoms have very similar electronegativities, so both C-H and C-C bonds are non-polar.
- As a result, cycloalkanes, like alkanes, are not a very reactive functional group.

**QUICK QUIZ-2**

**What are polar, no-polar and weakly polar compounds?**

**Polar Compounds**

The compounds in which electron density is unsymmetrical are called polar compounds.

In such compounds, electron density is more present on one side than other. Hence, positive and negative centers are developed within a molecule. e.g. water, methanol ( $CH_3OH$ ).

**Non-Polar Compounds**

The compounds in which electron density is symmetrical are called non-polar compounds.

In such compounds, electrons density is uniformly distributed throughout the molecule. Hence, positive and negative centers are not developed within a molecule e.g. carbon tetrachloride ( $CCl_4$ ), methane ( $CH_4$ ).

**Weakly****Polar Compounds**

The compounds in which electron density is slightly unsymmetrical are called weakly polar compounds.

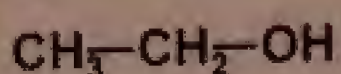
In such compounds, electron density is slightly more present on one side than other. Hence, weak positive and negative centers are developed within a molecule. e.g. acetone etc..

**What are isomers?**

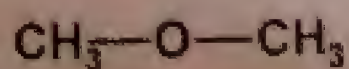
The compounds having same molecular formula but different structures and properties are called isomers and the phenomenon is called isomerism.

**Example:**

Ethanol and dimethyl ether are isomers of each other. Both have molecular formula  $C_2H_6O$  but different structures and properties.



Ethanol



Dimethyl ether

**What are inert compounds?**

The compounds which do not react under certain conditions are called inert compounds.



Examples:

- Noble gases such as He, Ne do not react with any compound. That is why they are called inert gases.
- Among organic compounds, alkanes have least reactivity. So, they do not react and remain inert in most of the conditions.

4. What is sigma bond?

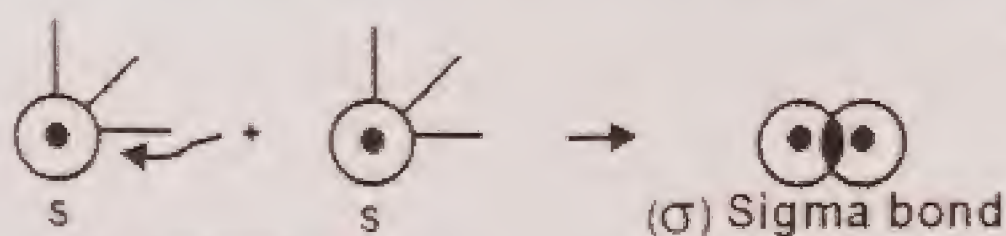
Any first bond formed between two partially filled orbitals is called a sigma bond

- It is formed by Head-on-overlap of orbitals.

In a sigma bond, the region of highest electron density is symmetrically distributed around the bond axis.

- The probability of finding the electron is maximum in the region between the two nuclei.

Example



5. What are intramolecular and intermolecular forces?

- The forces of attraction between separate molecules of substances are called intermolecular forces

Examples:

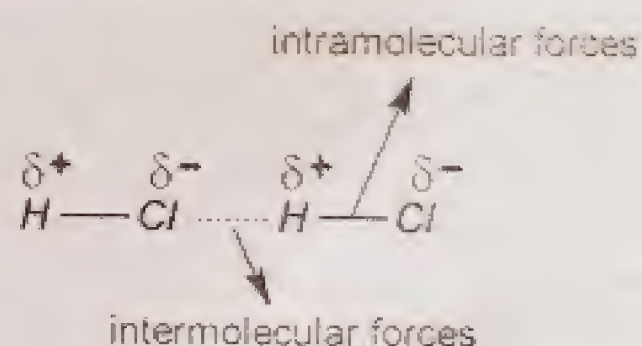
Dipole-Dipole forces, London dispersion forces etc.

- The forces of attractions between atoms within a molecule are called intramolecular forces.

Examples:

Chemical bonds i.e. ionic bond, covalent bond, co-ordinate covalent bond.

- Intramolecular forces are stronger than intermolecular forces.



## HOW TO DESCRIBE REACTION MECHANISM

- When reaction mechanisms are being described, a 'curly arrow' is sometimes used to show the movement of a pair of electrons.
- The beginning of the arrow shows where the electron pair starts from and the arrow head shows where the pair ends up. e.g.



- The arrows show that a pair of electrons is moving from the  $\text{Br}^-$  ion to the region between the bromine and the carbon. Thus a covalent bond is formed between the atoms.

The same reaction is shown again below, with all the bonding electrons indicated.





A half-arrow is used to show the movement of a single electron in reactions involving free radicals.

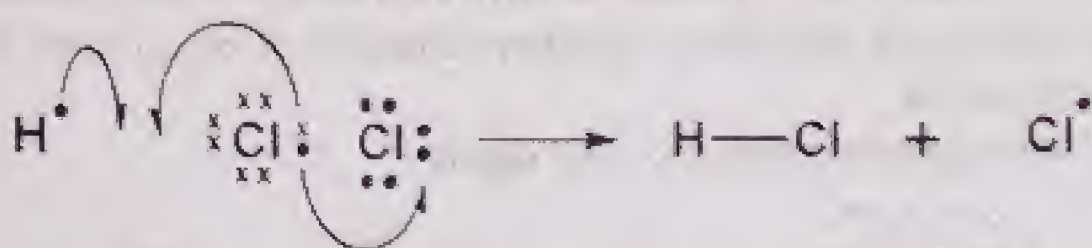
The beginning of the arrow shows where the single electron starts from and the half-arrow head shows where it ends up. e.g.,




It can be shown as

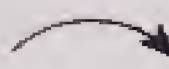



This is shown again below, with all the bonding electrons indicated.




**Summary of the way curly arrows and half-arrows are used.**

(1) Curly arrows  show the movement of an electron pair

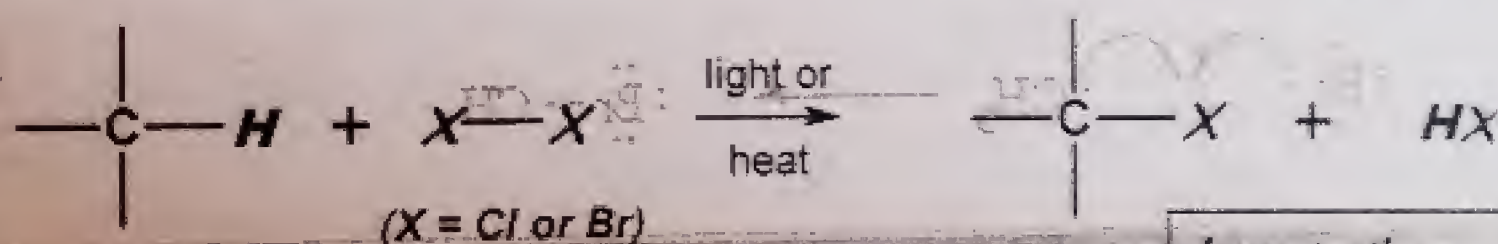
Electron pair starts here ...  ... finished here

(2) Curly half arrows  show the movement of a single, unpaired electron

Electron pair starts here ...  ... finished here

## RADICAL SUBSTITUTION REACTIONS

The substitution of hydrogen of an alkane molecule by a halogen atom takes place as below.

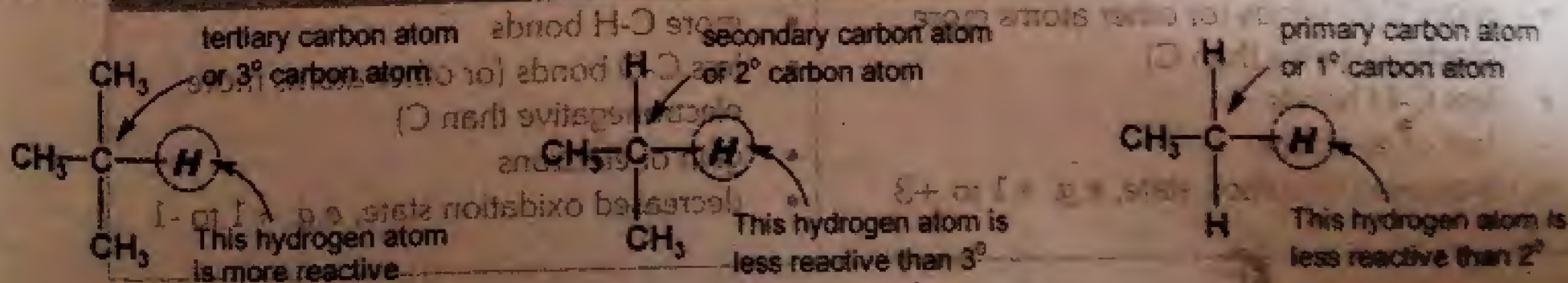


### Important to Note:

- Substitution of R-H by -X provides the alkyl halide, R-X and HX.
- Alkane R-H relative reactivity order:  $3^\circ > 2^\circ > 1^\circ > \text{methyl}$ .
- Halogen reactivity  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ .
- Only chlorination and bromination are useful in the laboratory.
- Reaction proceeds via a radical chain mechanism

### Important!

- $3^\circ$  is tertiary carbon (a carbon which is attached to three carbon atoms)
- $2^\circ$  is secondary carbon (a carbon which is attached to two carbon atoms)
- $1^\circ$  is primary carbon (a carbon which is attached to one carbon atom)





## REACTION MECHANISM: (Radical chain mechanism for reaction of methane with Br<sub>2</sub>)

### Step 1 (Initiation)

The weak halogen bond undergo homolytic cleavage Heat or UV light causes Thus it generates two bromine radicals and a chain process is started.



### Step 2 (Propagation)

(a) A bromine radical <sup>remove</sup> abstracts hydrogen from methane to form HBr and a methyl radical is formed.

(b) The methyl radical abstracts a bromine atom from another molecule of Br<sub>2</sub> to form the methyl bromide product and another bromine radical.

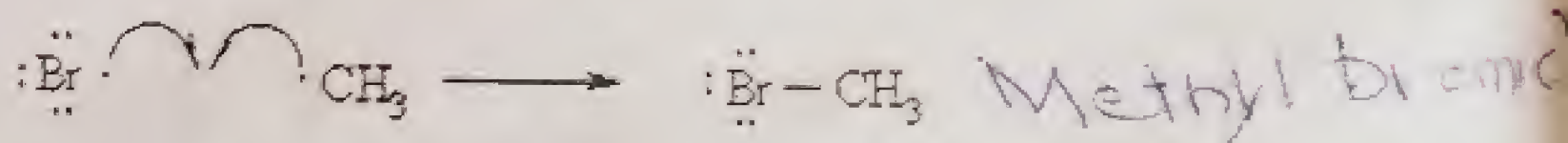
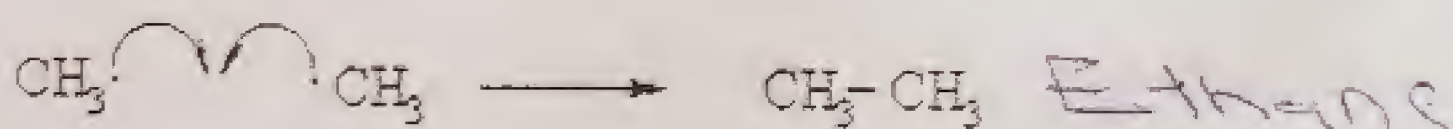
Both these steps (a) and (b) are repeated over and over again



### Step 3 (Termination)

Various reactions between the possible pairs of radicals form ethane, Br<sub>2</sub> or methyl bromide.

- These reactions remove radicals and do not continue the cycle.



## OXIDATION AND REDUCTION OF ORGANIC COMPOUNDS

- Oxidation, [O], and reduction, [R], are opposites to each other. Both these occur simultaneously, hence these reactions are called **redox reactions**.
- Organic chemists will normally describe a reaction as either oxidation or reduction depending on the fate of the major organic component.

Oxidation	Reduction
<ul style="list-style-type: none"> <li>more C-O bonds (or other atoms more electronegative than C)</li> <li>less C-H bonds</li> <li>loss of electrons</li> <li>increased oxidation state, e.g. +1 to +3</li> </ul>	<ul style="list-style-type: none"> <li>more C-H bonds</li> <li>less C-O bonds (or other atoms more electronegative than C)</li> <li>gain of electrons</li> <li>decreased oxidation state, e.g. +1 to -1</li> </ul>

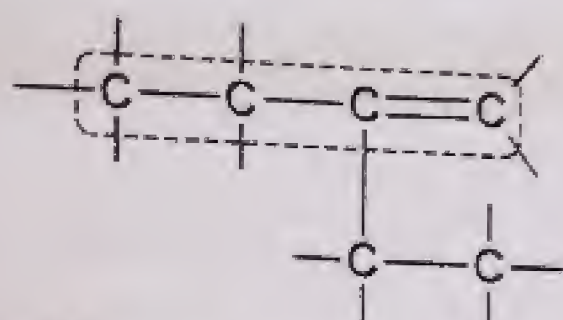


# ALKENES

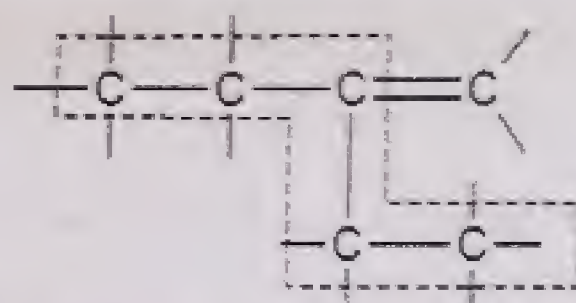
Acyclic unsaturated hydrocarbons containing double bond are called alkenes.

## NOMENCLATURE:

- (1) The longest continuous chain containing double bond is selected as parent chain.
- (2) The ending 'ane' is replaced by 'ene'.

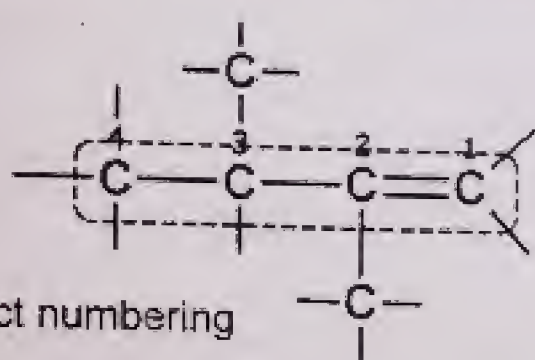


Longest Chain with double bond (Correct)

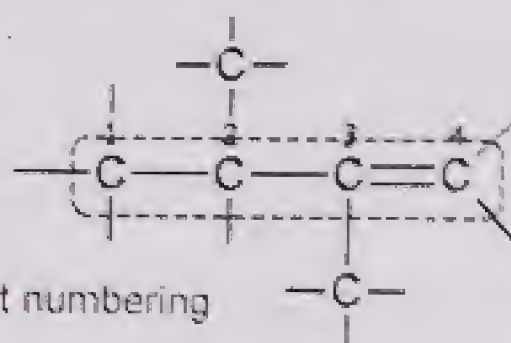


Longest Chain without double bond (Incorrect)

- (3) The chain is numbered in such a manner as to give minimum number to the doubly bonded C-atoms.

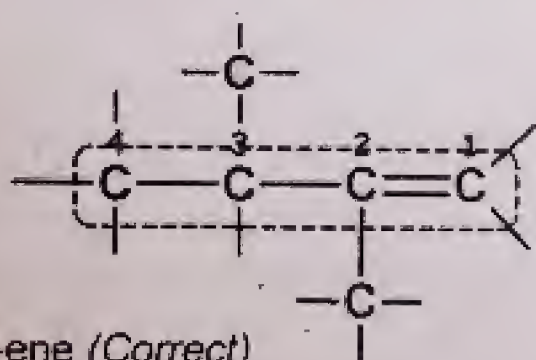


Correct numbering

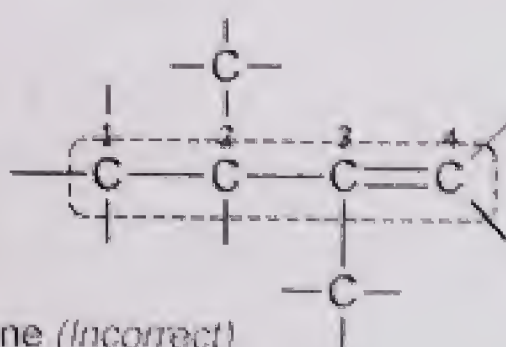


Incorrect numbering

- (4) The position of double bond is indicated by the lower number of C-atom.



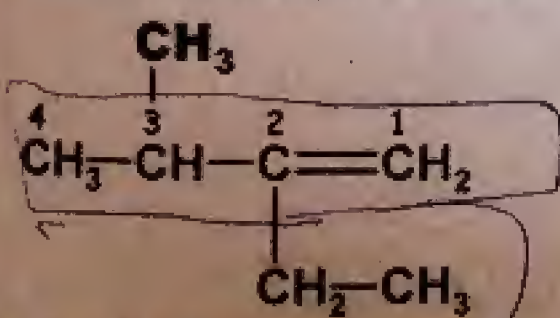
1-ene (Correct)



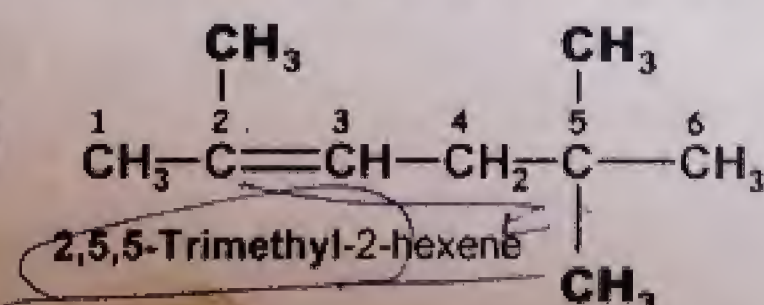
2-ene (Incorrect)

- (5) The lower number of C-atom is placed before the name of parent alkene.

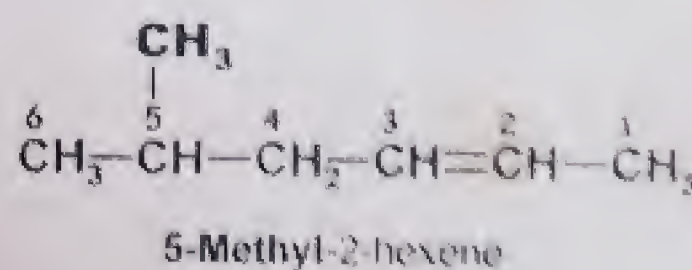
- (6) Alkyl groups are indicated by the methods mentioned in alkane.



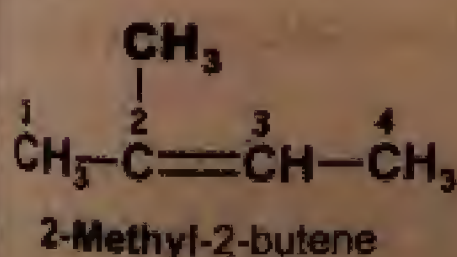
2-Ethyl-3-methyl-1-butene



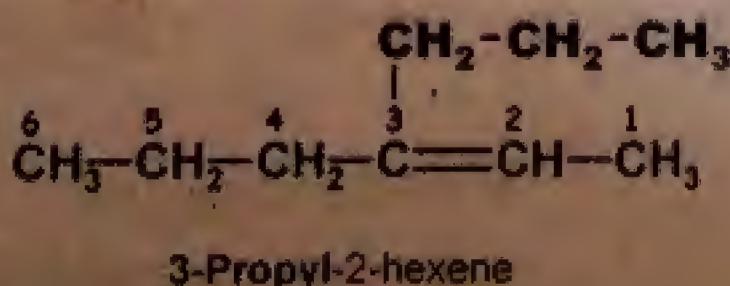
2,5,5-Trimethyl-2-hexene



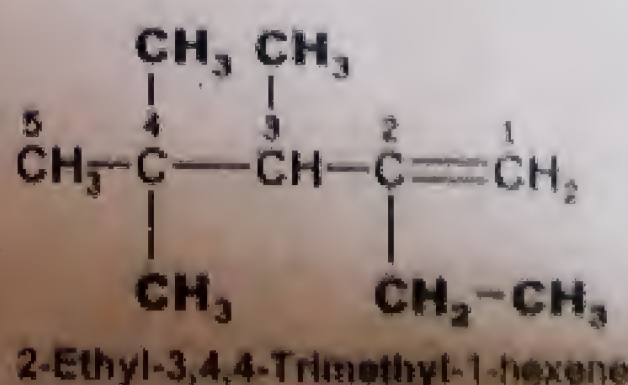
5-Methyl-2-hexene



2-Methyl-2-butene



3-Propyl-2-hexene



2-Ethyl-3,4,4-Trimethyl-1-hexene



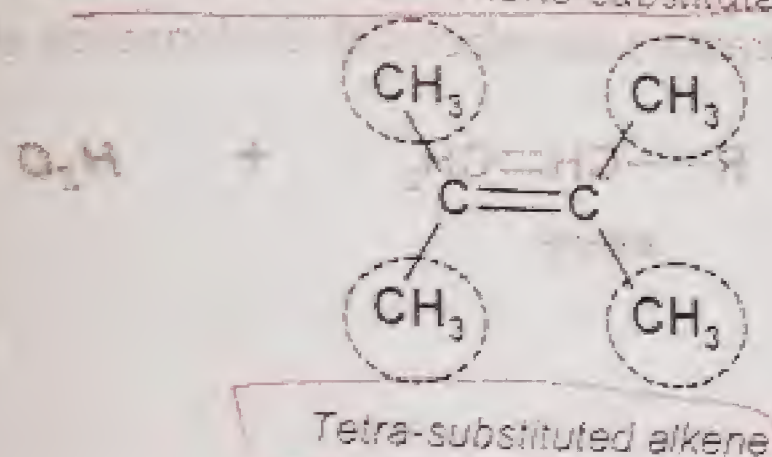




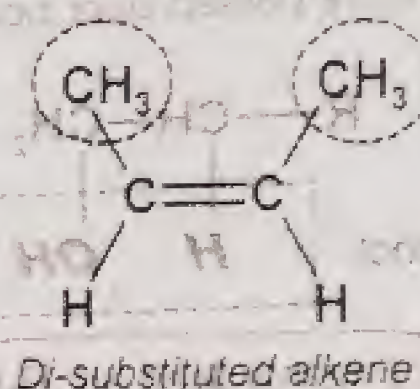
## RELATIVE STABILITY

There are three factors that influence alkene stability:

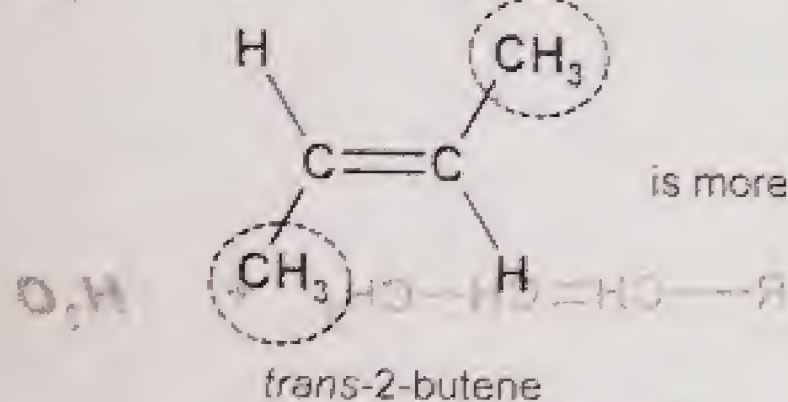
- (1) Degree of substitution: more highly alkylated alkenes are more stable, so tetra > tri > di > mono-substituted.



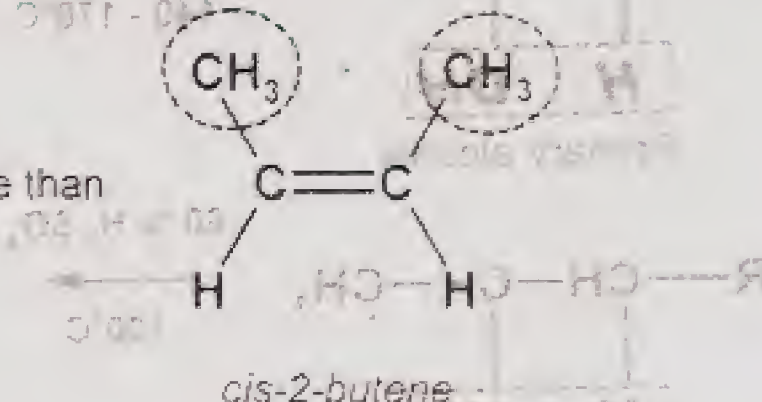
is more stable than



- (2) Stereochemistry: trans > cis due to reduced steric interactions when R groups are on opposite sides of the double bond. e.g. trans-2-butene > cis-2-butene



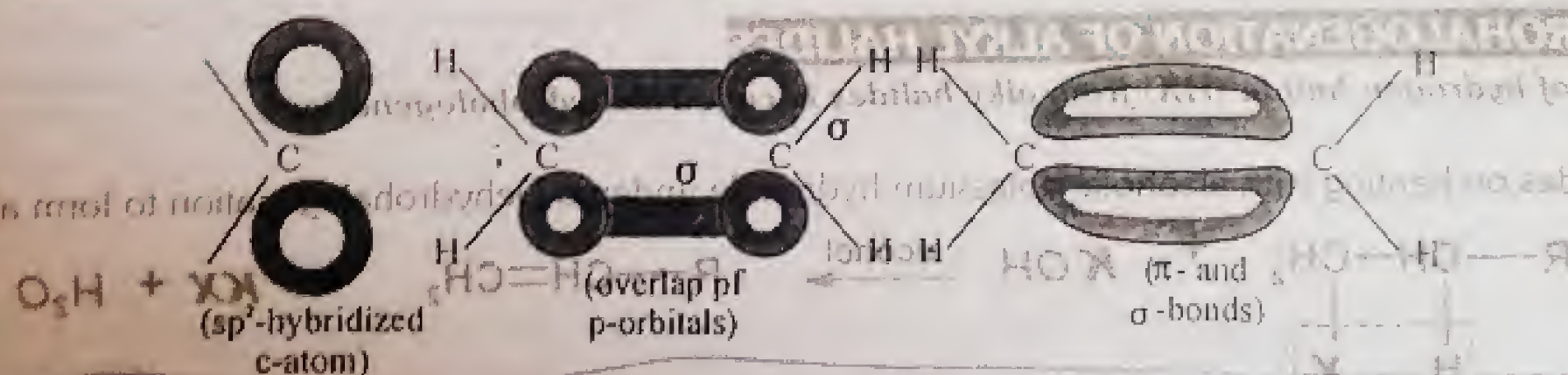
is more stable than



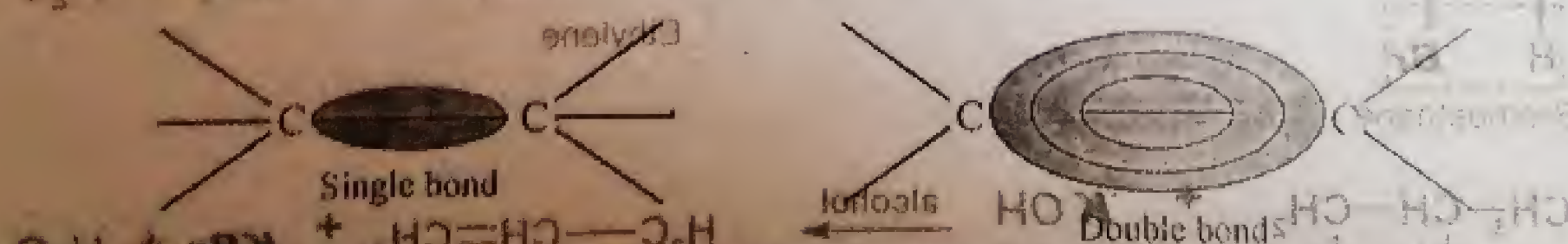
- (3) Conjugated alkenes are more stable than isolated alkenes. 1,3-Pentadiene is more stable than 1,4-pentadiene

## STRUCTURE

- The carbon atoms joined together by  $\pi$ -bond are  $sp^2$  hybridized.
- Thus, each carbon atom has three  $sp^2$ -hybrid orbitals and one p-orbital.
- The hybrid orbitals form  $\sigma$ -bonds due to linear overlap.
- The p-orbitals form  $\pi$ -bond due to sideways overlap.



- The carbon-carbon distance in ethene is shorter ( $1.34\text{\AA}$ ) than the C-C bond distance of ethane ( $1.54\text{\AA}$ ). It is due to increased electron density between carbon atoms.



- Carbon atoms are coplanar, and the rotation of one C-atom with respect to other is restricted which results in cis-trans isomerism in alkene.



## PREPARATION OF ALKENES

### (1) DEHYDRATION OF ALCOHOLS

Removal of water molecule is called dehydration.

Example

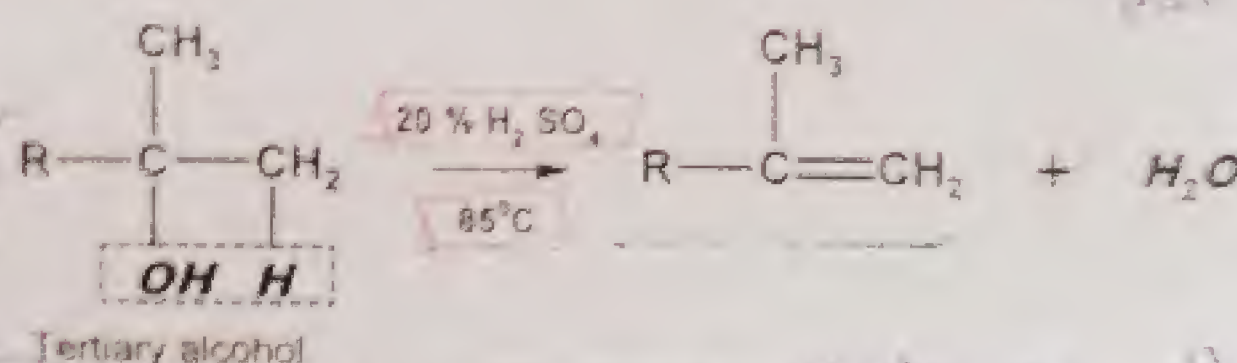
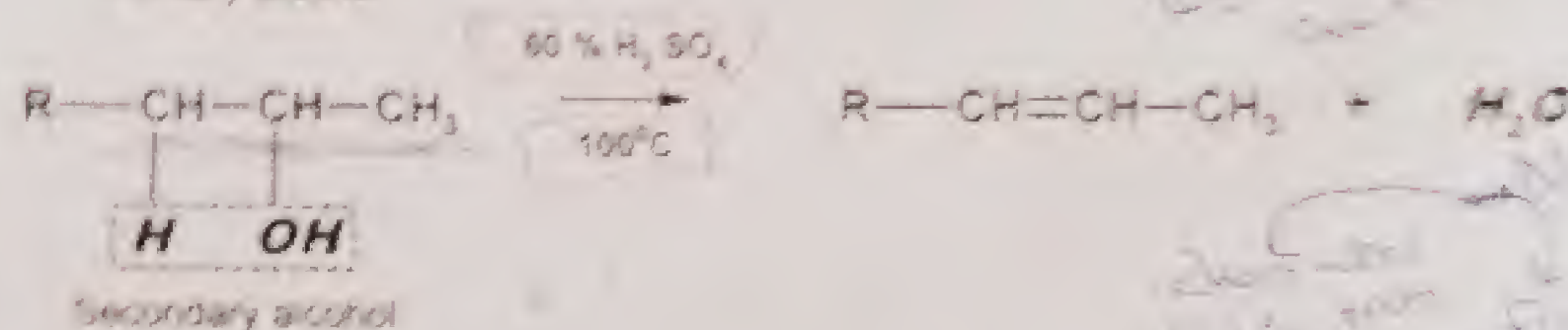
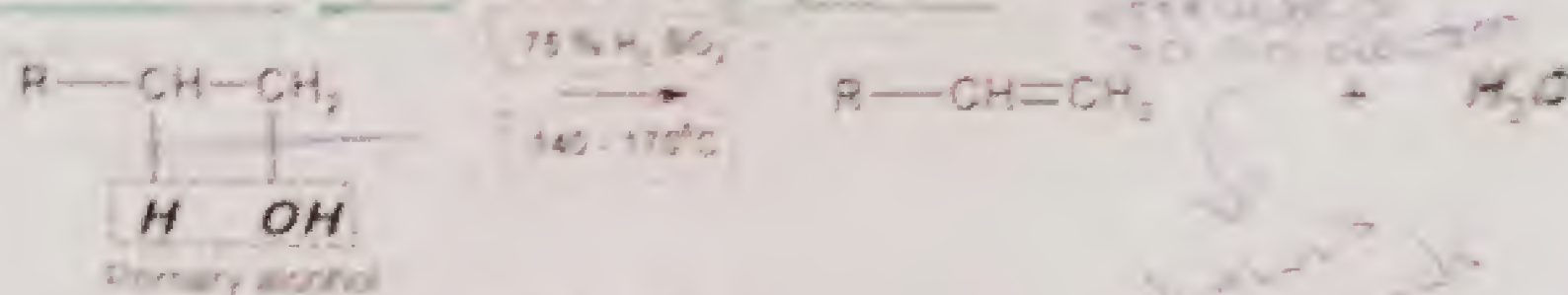
When vapours of alcohol are passed over heated alumina, dehydration takes place with the formation of alkene.



Other dehydrating agents used are  $\text{P}_2\text{O}_5$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HPO}_3$ .

The ease of dehydration of various alcohols is in the order:

Tertiary alcohol > secondary alcohol > primary alcohol

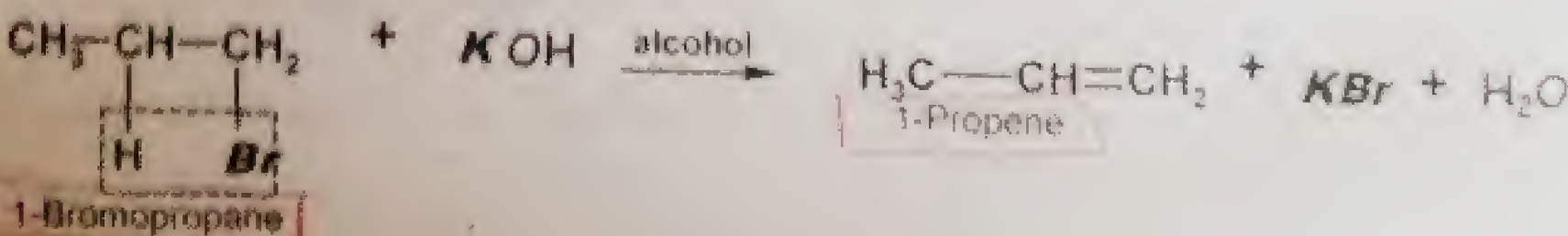
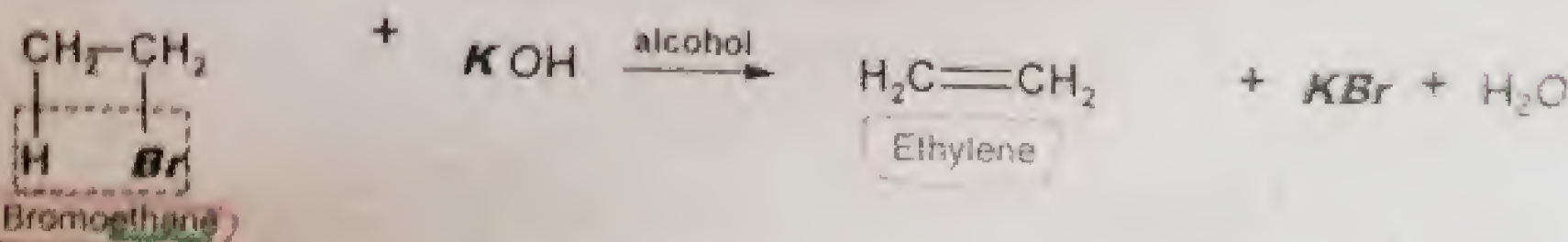
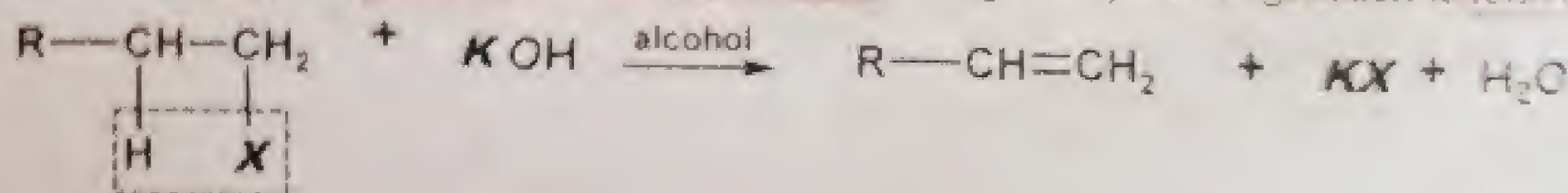


### (2) DEHYDROHALOGENATION OF ALKYL HALIDES

Removal of hydrogen halide (HX) from alkyl halides is called Dehydrohalogenation.

Example

Alkyl halides on heating with alcoholic potassium hydroxide undergo Dehydrohalogenation to form alkenes.





## ACTIVITY and REACTIONS:

There is a relatively diffuse region of high electron density in alkenes as compared to alkanes.

This is due to  $\pi$ -bonds in alkenes. Since an ethene  $\pi$ -bond is weaker than  $\sigma$ -bond, it requires less energy to break a  $\pi$ -bond.

Hence the reactions of alkenes involve weaker  $\pi$ -bond and electrophilic addition occurs.

It involves the change of a  $\pi$ -bond to sigma bond through addition reactions.

## HYDROGENATION

A process in which a molecule of hydrogen is added to an alkene in the presence of a catalyst and at moderate pressure (1-5 atm) to give a saturated compound is known as catalytic hydrogenation.

Examples and Explanation:

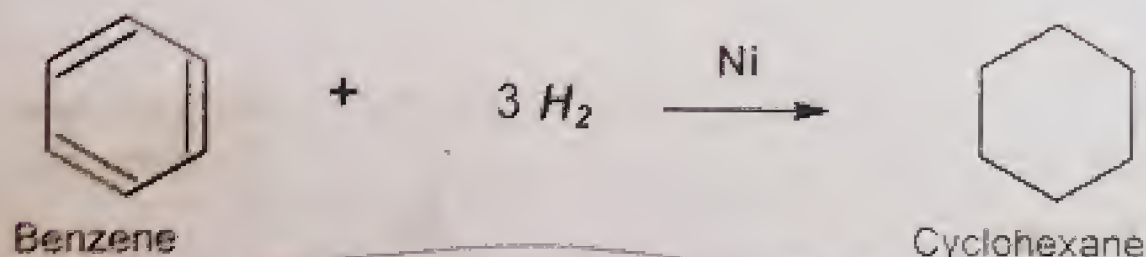
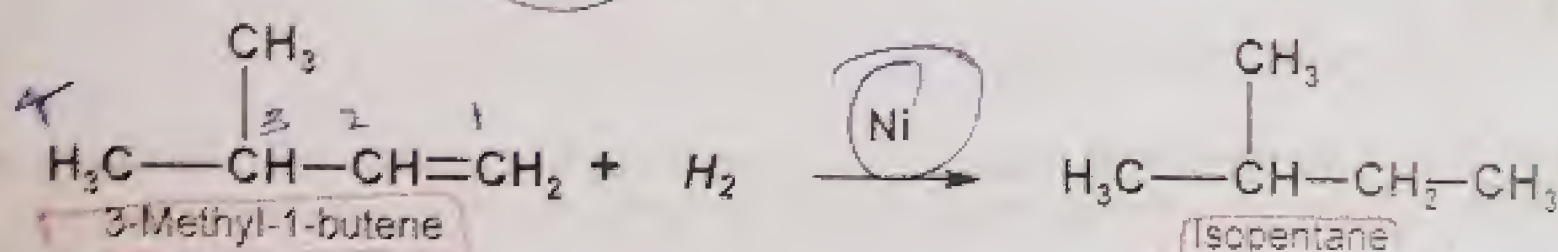
- It is a highly exothermic process and the amount of heat evolved when one mole of an alkene is hydrogenated is called Heat of Hydrogenation.
- The heat of hydrogenation of most alkene is about  $120 \text{ kJ mole}^{-1}$  for each double bond present in a molecule.
- The catalysts employed are Pt, Pd and Raney Nickel.

Raney Nickel: is a catalyst of hydrogenation.

It is prepared by treating a Ni-Al alloy with caustic soda.



Examples:



- Reaction
- Catalyst
- Temperature pressure

Catalytic hydrogenation has many applications

In industry, vegetable ghee is prepared by catalytic hydrogenation of vegetable oil.

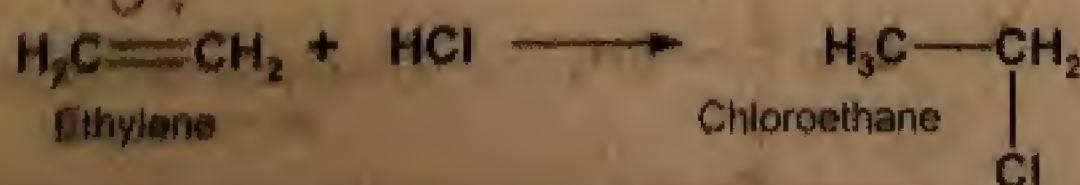
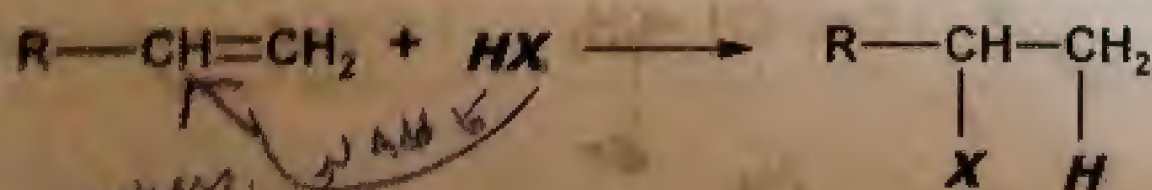
The reaction is quantitative, therefore, it is used in laboratory for analytical purpose.

It is also used as synthetic method in laboratory.

## HYDROHALOGENATION

the electrophilic addition of

Alkenes react with aqueous solution of halogen acid to form alkyl halides.



hydrohalic acids to alkene  
composed of hydrogen & halogen

The order of reactivity of halogen acids is  $\text{HI} > \text{HBr} > \text{HCl}$

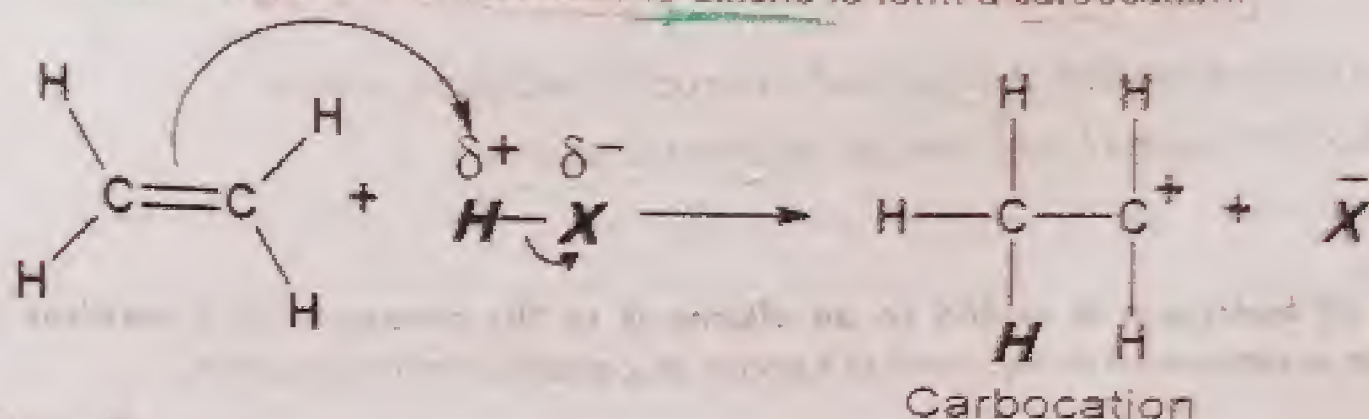


### Mechanism

The process occurs in two steps

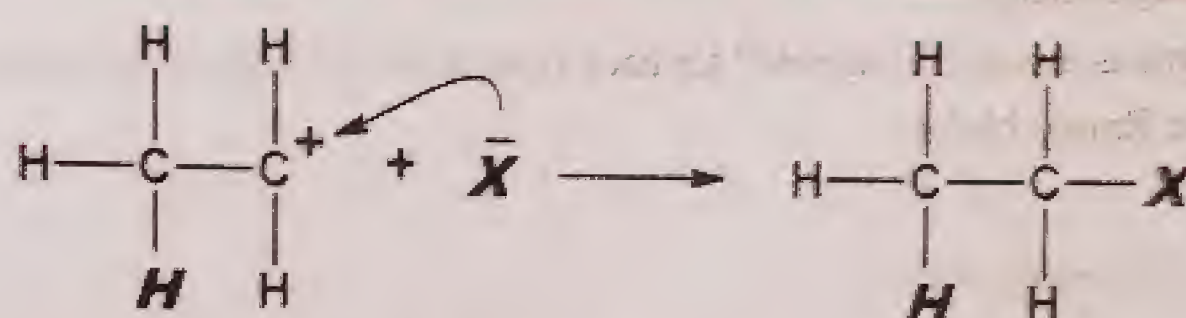
#### Step - 1

In first step, proton of HX adds to alkene to form a carbocation.



#### Step - 2

In second step, halide ion combines with carbocation to give alkyl halide.



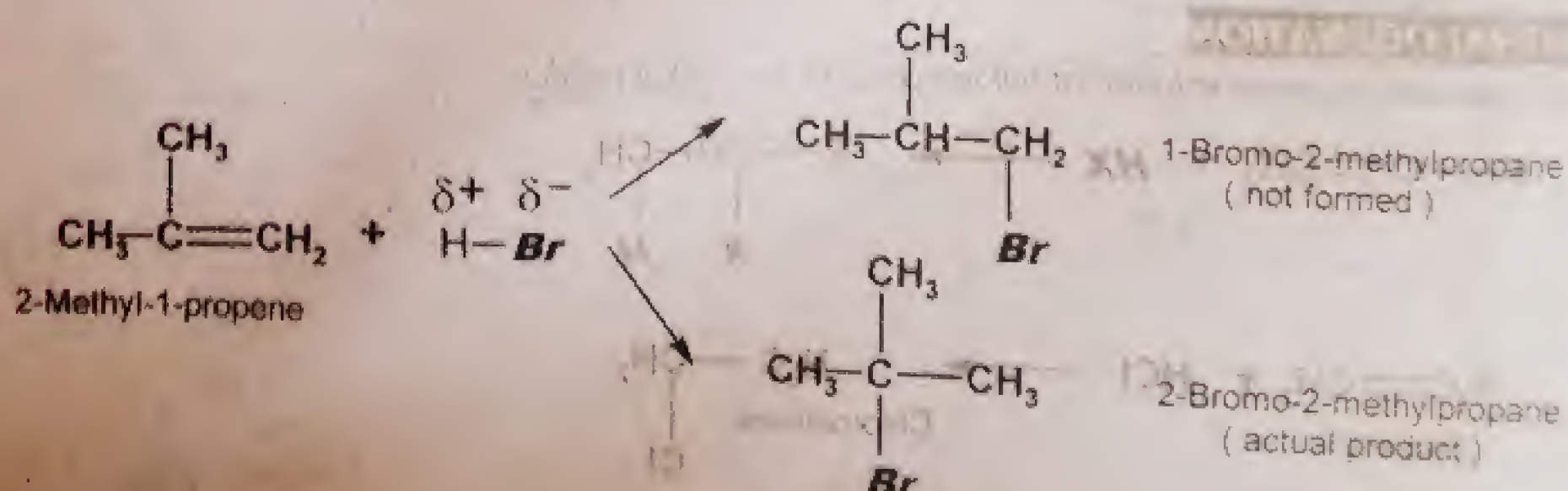
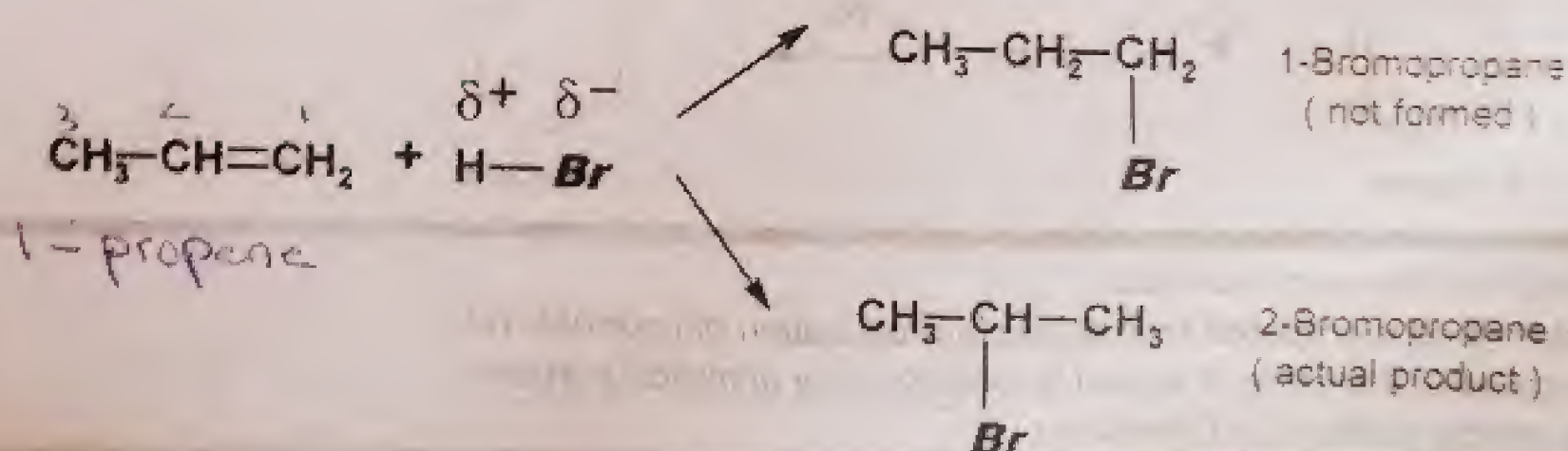
### Markownikov's Rule

The addition of HX to unsymmetrical alkenes follows Markownikov's Rule.

It states

In the addition of an unsymmetrical reagent to an unsymmetrical alkene, the negative part of the added reagent goes to that carbon, consisting the double bond, which has least number of hydrogen atoms.

Examples:

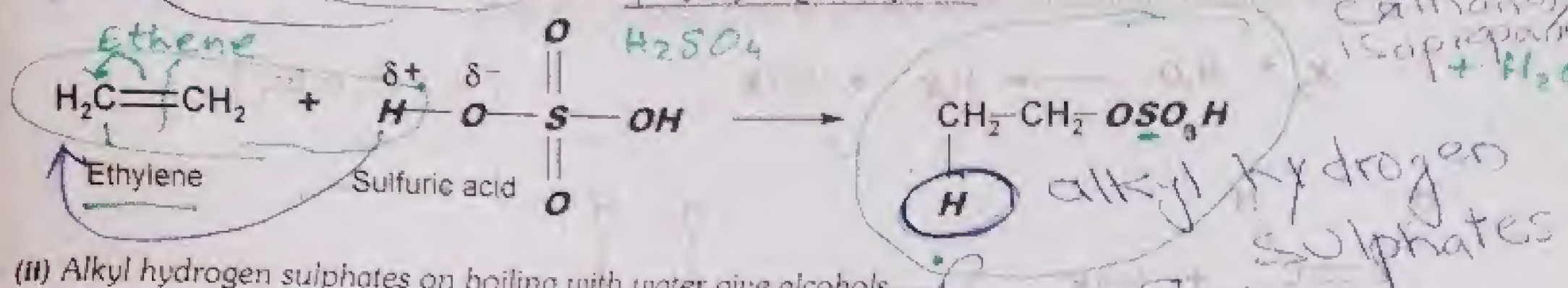




### 3) HYDRATION

Some reactive alkenes react with water in the presence of suitable substances as acid etc. to form alcohol. It is possible as alkenes are soluble in cold concentrated sulfuric acid. The reaction occurs in two steps

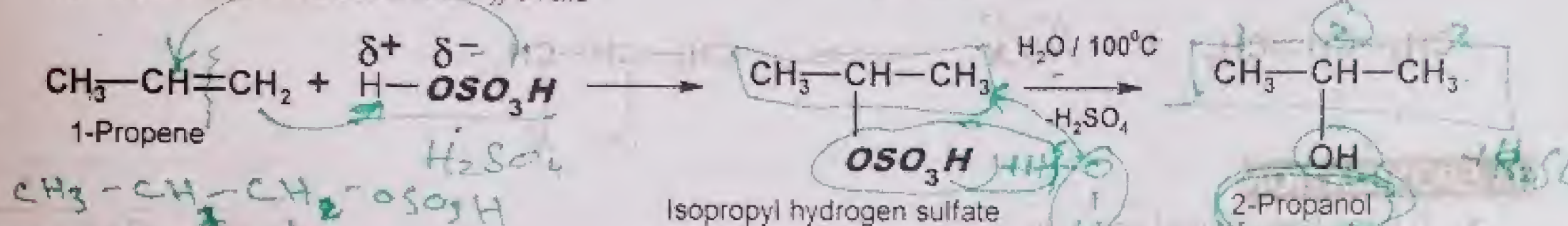
(i) Alkenes dissolve in conc.  $H_2SO_4$  and form alkyl hydrogen sulphates.



(ii) Alkyl hydrogen sulphates on boiling with water give alcohols.



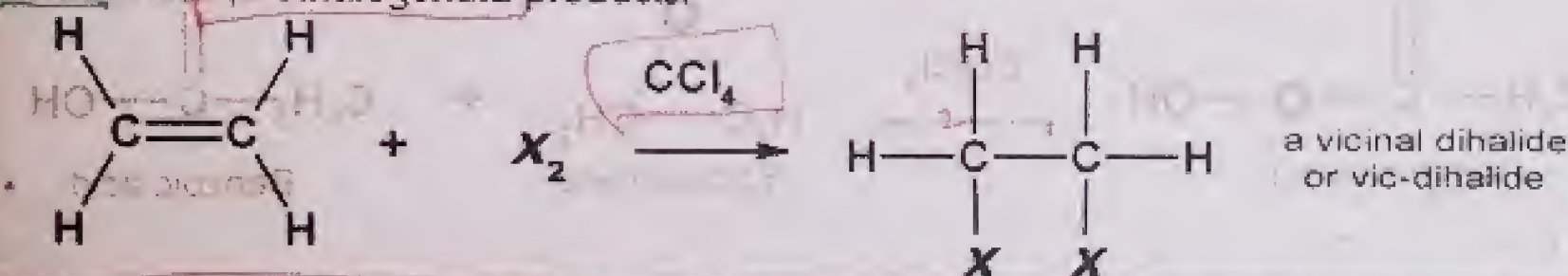
The reaction follows Markovnikoff's rule



### (4) HALOGENATION

Test with a halogen

The alkenes react with halogen in an inert solvent like carbon tetrachloride at room temperature to give vicinal dihalides or 1,2 dihalogenated products.



Remember!

A vicinal or vic-dihalide has two halogen atoms on adjacent carbon atoms

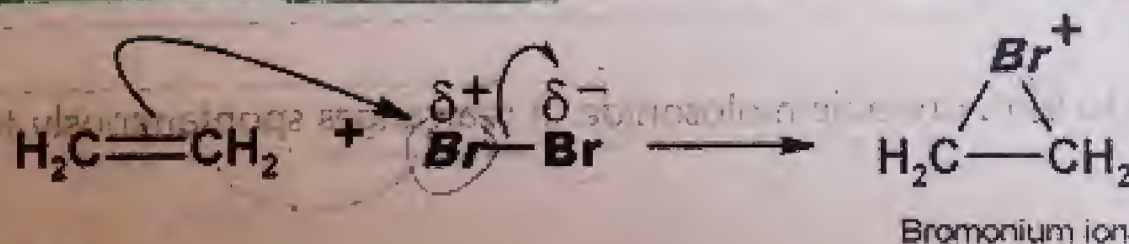
$Br_2$  and  $Cl_2$  are effective electrophilic reagents. Reaction of  $F_2$  is too fast to control.  $I_2$  does not react.

#### Mechanism

The reaction occurs in two steps

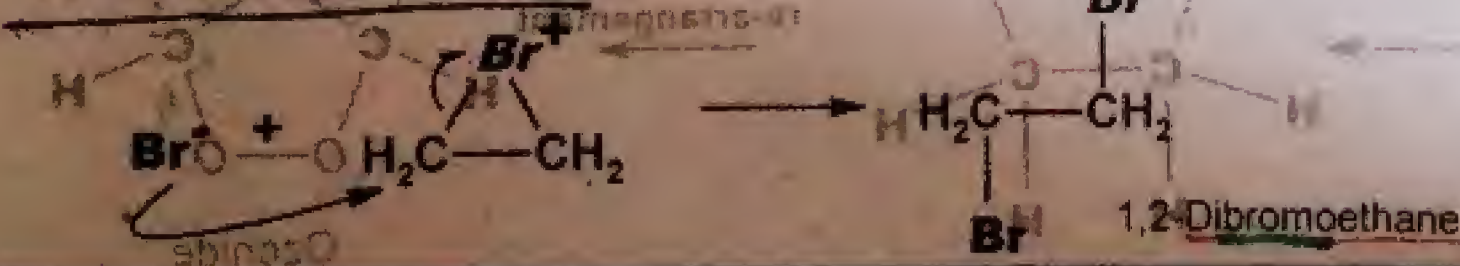
##### Step - 1

A bromine molecule becomes polarized as it approaches the alkene. This polarized bromine molecule transfers a positive bromine atom to the alkene resulting in the formation of a bromonium ion.



##### Step - 2

The nucleophilic bromide ion then attacks on the carbon of the bromonium ions to form vic-dibromide and the color of bromine is discharged.



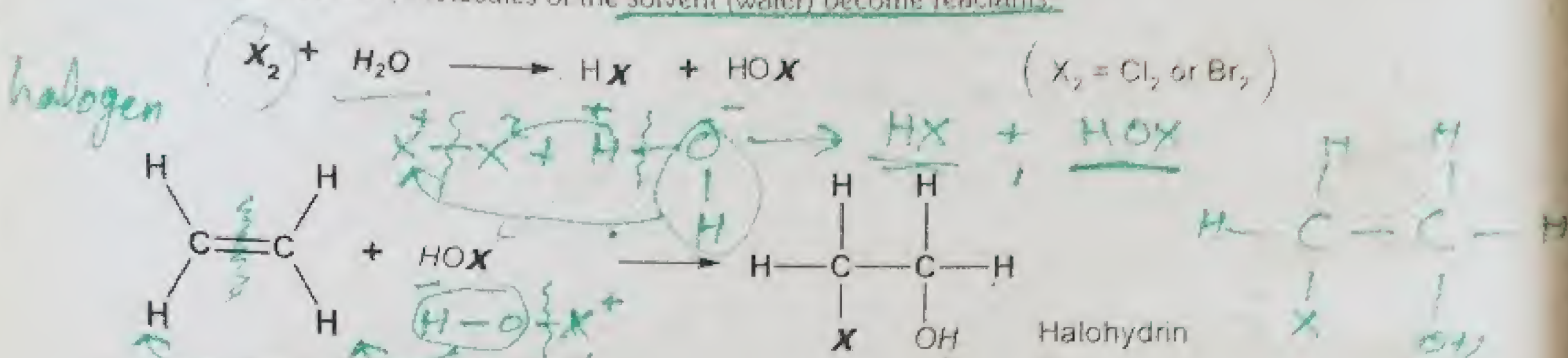
In this reaction red colour of  $Br_2$  is discharged. So this reaction is used to detect the presence of double bond in a compound.



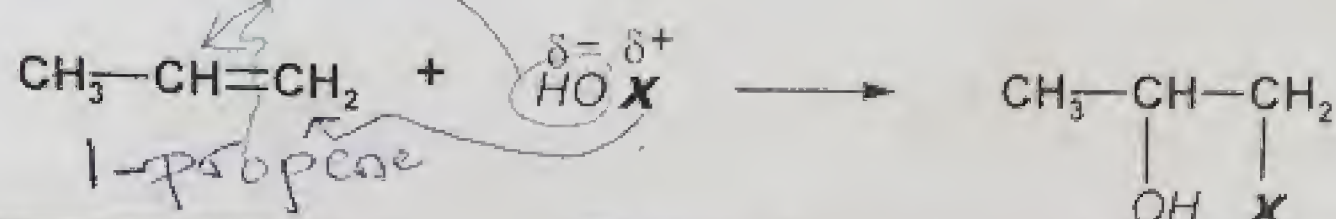
## (5) HALOHYDRATION

Addition of hypohalous acid (HOX) is called halohydrin.

- Alkenes react with hypohalous acid to give Halohydrin.
- In this reaction, molecules of the solvent (water) become reactants.

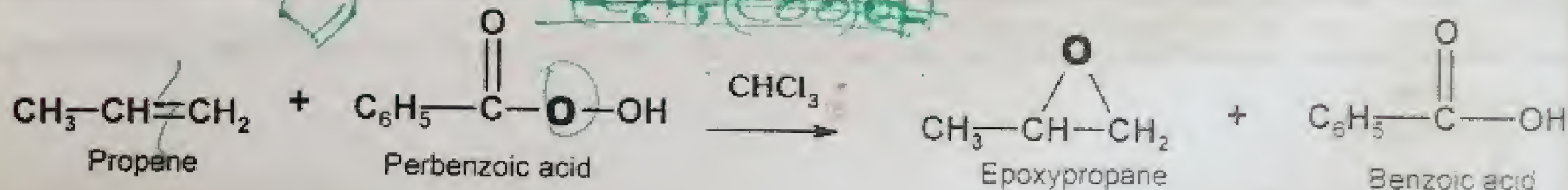
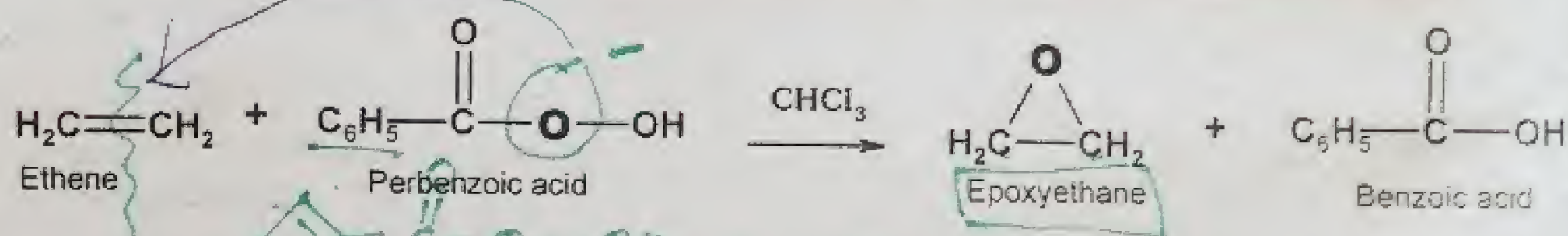


The reaction follows Markownikoff's rule.



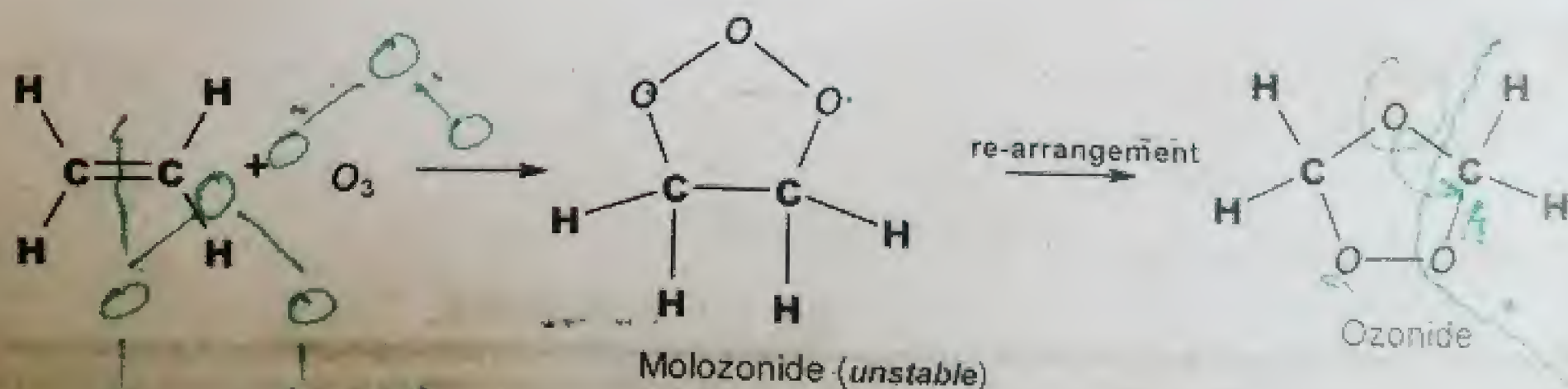
## (6) EPOXIDATION

- It is the formation of epoxides.
- Peracids such as peroxyacetic acid or peroxybenzoic acids react with alkenes to form epoxides.



## (7) OZONOLYSIS

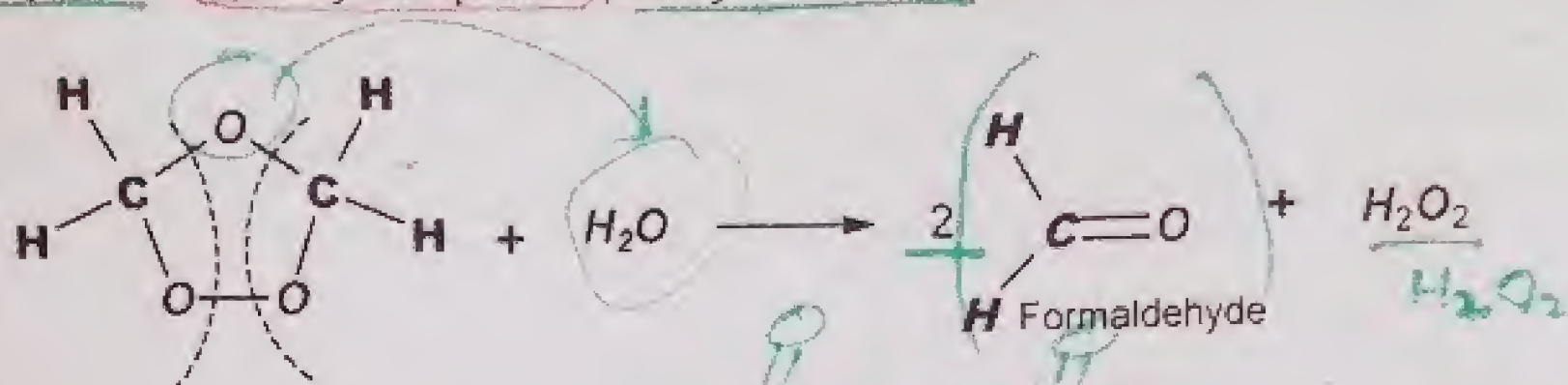
Ozone ( $O_3$ ) reacts vigorously with alkenes to form unstable molozonide. It rearranges spontaneously to form an ozonide.





## REDUCTION OZONIDE

Ozonides are unstable compounds and are reduced directly on treatment with zinc and  $H_2O$ . The reduction produces carbonyl compounds (aldehydes or ketones).

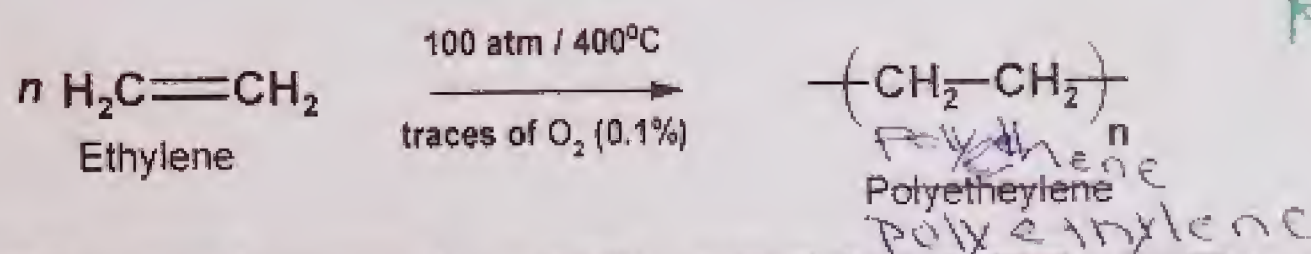


- Ozonolysis is used to locate the position of double bond in an alkene.
- The C-atom of double bond is changed to carbonyl group.

## POLYMERIZATION

Polymerization is a process in which a small organic molecules which are called monomers combine together to form larger molecules. The substances so produced are called polymers.

Ethene polymerizes to polythene at  $400^\circ\text{C}$  at a pressure of 100 atm.

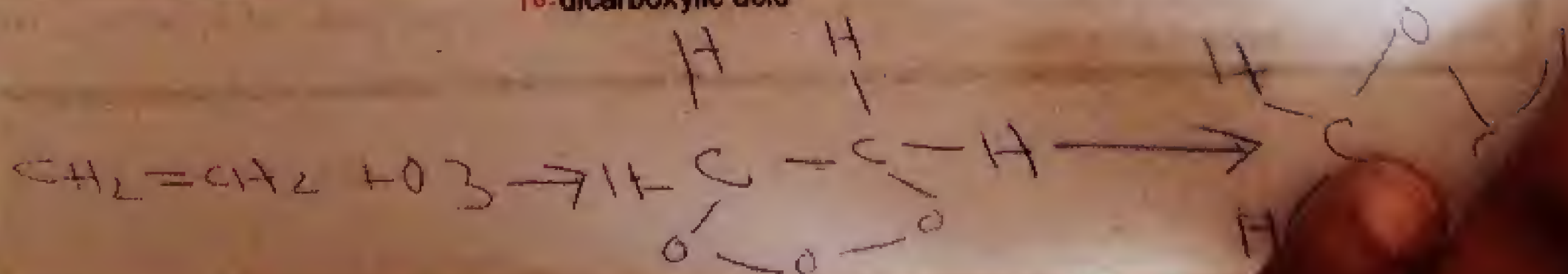


Good quality of polyethylene is also produced by polymerization of ethene in the presence of aluminium triethyl  $\text{Al}(\text{C}_2\text{H}_5)_3$  and titanium tetrachloride  $(\text{TiCl}_4)$  catalysts.

## Interesting Information

### Examples of natural and synthetic polymers

	Polymer	Monomer	Where you find it
Natural	1. Protein	1. Amino acids	1. Wool, silk, muscle, etc
	2. Starch	2. Glucose	2. Potato, wheat, etc
	3. Cellulose	3. Glucose	3. Paper, wood, dietary fibre chromosomes, genes
	4. DNA	4. Nucleotides	4. Bags, washing-up bowls, etc
	5. Poly (ethane)	5. Ethane	5. Fabric coatings, electrical insulation, toys, expanded polystyrene
Synthetic	6. Poly (chloroethene)	6. Chloroethene	6. Skirts, shirts, trousers
	7. (PVC)	7. Phenylethene	
	8. Poly (phenylethene)		
	9. (polystyrene)	6. Ethane-, 2-diol and	
	10. polyester	9. benzene- 1, 2-dicarboxylic acid	





CH #16: Hydrocarbons

$A = B \xrightarrow{\text{bonds}} X$  conjugation is the sequence of  
as = double single

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College Chemistry: Federal Board, Part-II

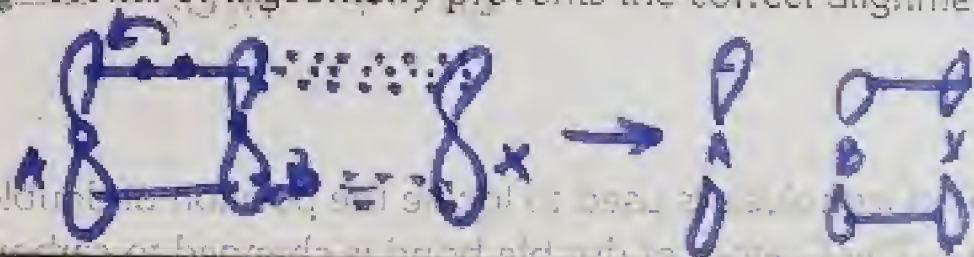
## CONJUGATION

- The word "conjugation" is derived from a Latin word that means "to link together".
- In organic chemistry, it is used to describe the situation that occurs when p-systems are "linked together".
- An "isolated" p-system exists only between a single pair of adjacent atoms (e.g.  $C=C$ ).
- An "extended" p-system exists over a longer series of atoms (e.g.  $C=C-C=C$  or  $C=C-C=O$  etc.).
- An extended p-system results in an extension of the chemical reactivity.

### Fundamental Condition of a Conjugated System

- A conjugated system requires that there is a continuous array of "p" orbitals that can align to produce a bonding overlap along the whole system.
- If a position in the chain does not provide a "p" orbital or if geometry prevents the correct alignment, then the conjugation is broken at that point.

Examples:



System	p system	Type	System	p system	Type
Ethene		isolated	1,4-Pentadiene		isolated
Propene		isolated	1,3-Cyclopentadiene		conjugated
1,2-Propadiene (Allene)		cumulated	1,3-Cyclohexadiene		conjugated
1,3-Butadiene		conjugated	1,4-Cyclohexadiene		isolated
1,3-Pentadiene		conjugated	Benzene		conjugated

The result of conjugation is that there are extra p bonding interactions between the adjacent p systems that results in an overall stabilization of the system.

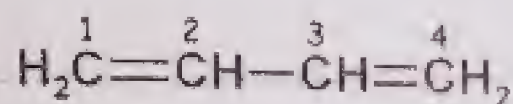


\* Delocalization of conjugated pi electrons have alternative double bonds

### QUICK QUIZ-3

**What is Conjugation?** → The movement of a charge from one atom to another is called delocalization.  
The word "conjugation" is derived from a Latin word that means "to link together".  
In organic chemistry, it is used to describe the situation that occurs when p-systems are "linked together". Thus an "extended" p-system exists over a longer series of atoms [e.g.  $C=C-C=C$  or  $C=C-C=O$  etc.]

Example:



1,3-Butadiene



**What are conjugated alkenes?**

The alkenes in which an "extended" p-system exists over a longer series of atoms [e.g.  $C=C-C=C$ ]

Example



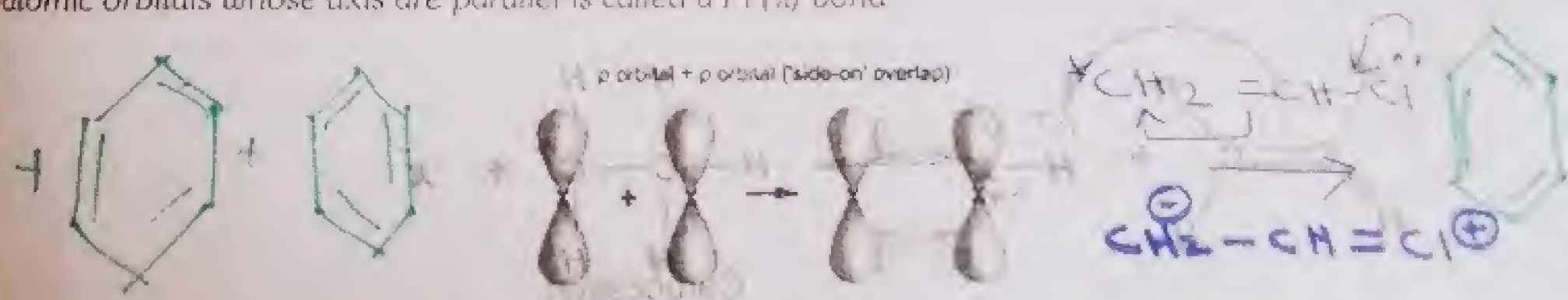
1,3-Butadiene



1,3,5-Hexatriene

**What is pi bond**

A bond formed between two already  $\sigma$  bonded atoms by the sidewise overlap of their two half-filled p-atomic orbitals whose axis are parallel is called a Pi ( $\pi$ ) bond



$\pi$ -bond formation

**What are s and p orbitals**

When the value of azimuthal quantum number is 0 ( $l = 0$ ), then it is called s subshell. It has spherical shape. It can have maximum two electrons.

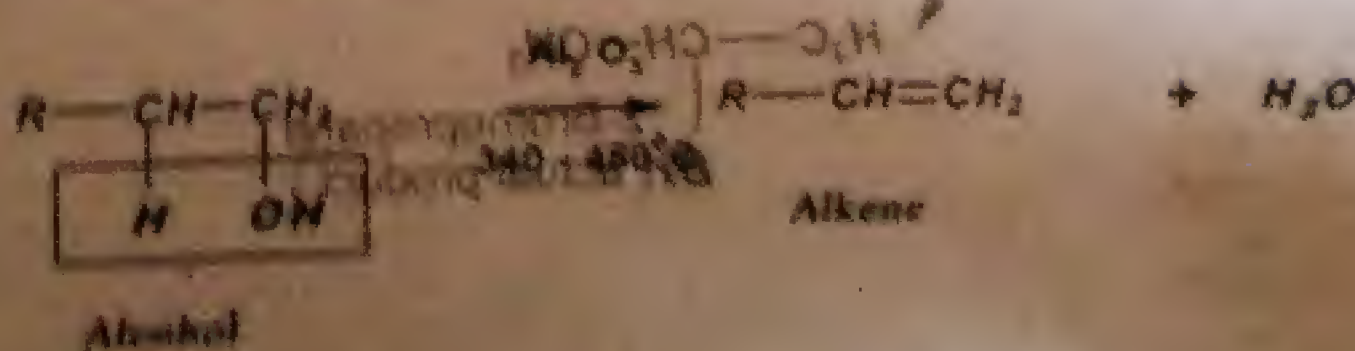
When the value of azimuthal quantum number is 1 ( $l = 1$ ), then it is called p subshell. The p subshell has three orbitals  $p_x$ ,  $p_y$  and  $p_z$ . These orbitals are present along X, Y and Z axis respectively. The  $p_x$  and  $p_y$  orbitals can have maximum two electrons each. Thus, p-subshell can have total six electrons.

**What is dehydration**

Removal of water molecule is called dehydration.

Example

When vapors of alcohol are passed over heated alumina, dehydration takes place with the formation of alkene.



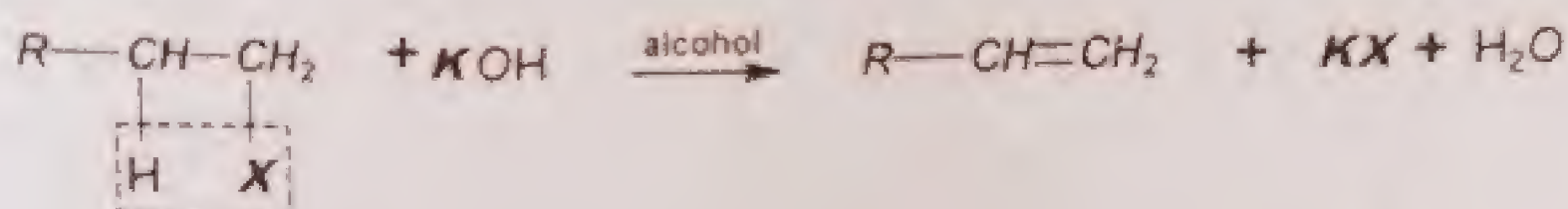


### 6. What is dehydrohalogenation

Removal of hydrogen halide (HX) from alkyl halides is called Dehydrohalogenation

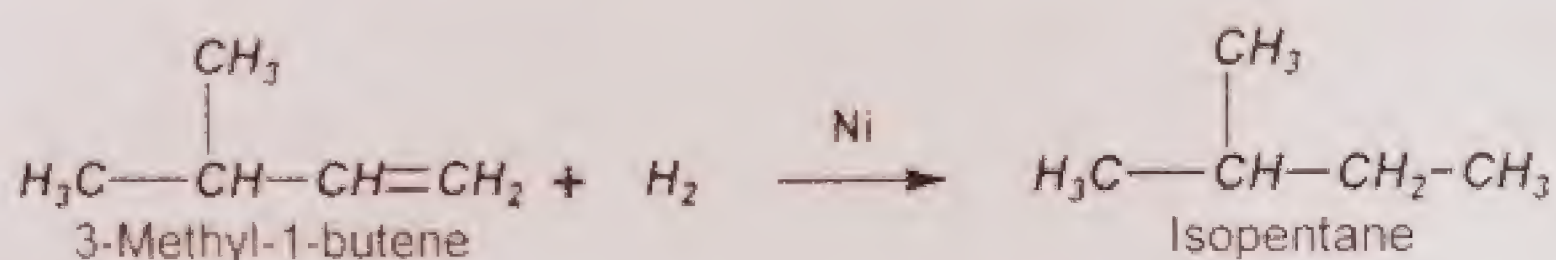
#### Example

Alkyl halides on heating with alcoholic potassium hydroxide undergo Dehydrohalogenation to form alkenes



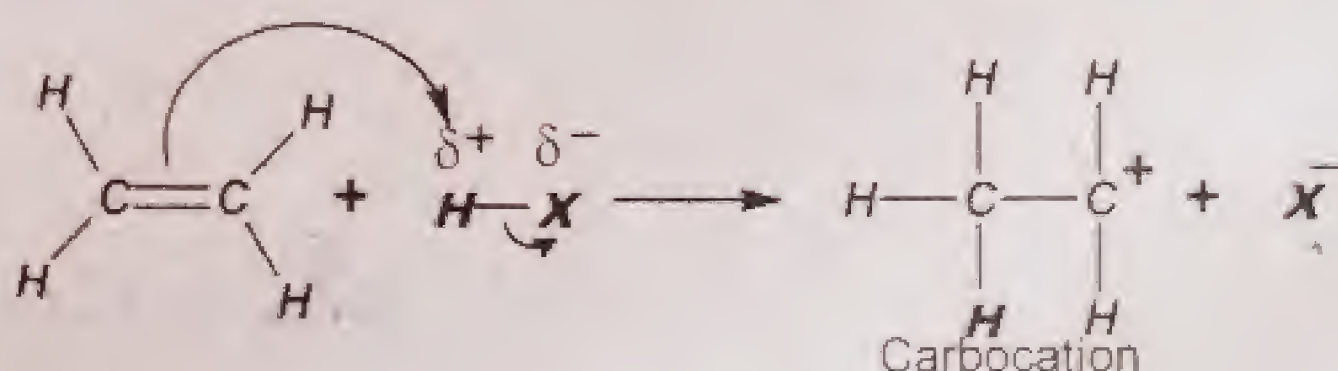
### 7. What is hydrogenation

A process in which a molecule of hydrogen is added to an alkene in the presence of a catalyst and moderate pressure (1-5 atm) to give a saturated compound is known as catalytic hydrogenation.



### 8. What is carbocation

A carbocation is a reaction intermediate. It is trivalent with a positive charge on carbon atom. It can be produced as follows

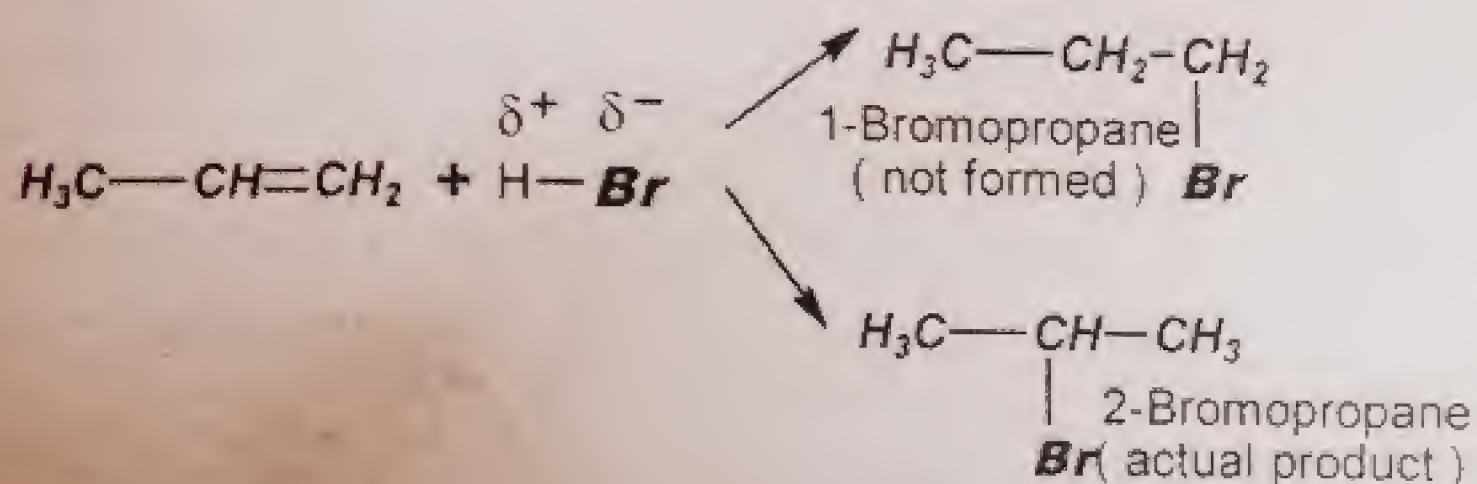


### 9. What is Markownikov's rule?

It states

In the addition of an unsymmetrical reagent to an unsymmetrical alkene, the negative part of the adding reagent goes to that carbon, consisting the double bond, which has least number of hydrogen atoms.

#### Example:





**10. What is electrophilic reagent?**

An electron deficient reagent is called an electrophilic reagent. e.g.  $\text{AlCl}_3$ ,  $\text{BF}_3$  etc.

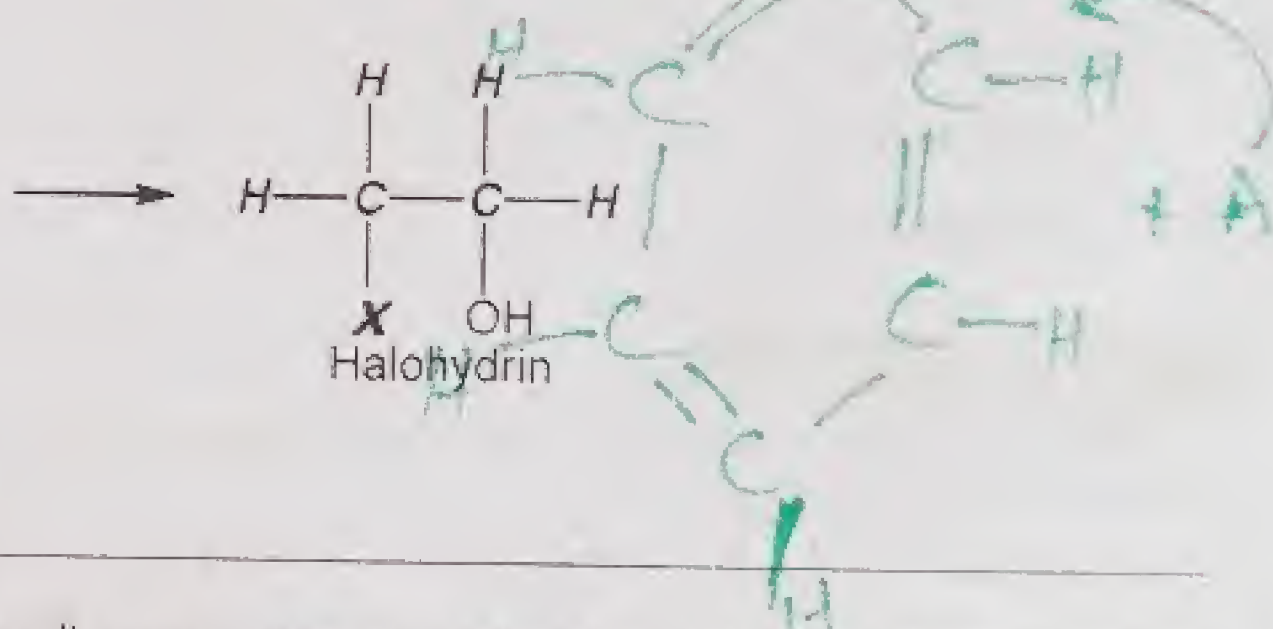
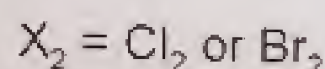
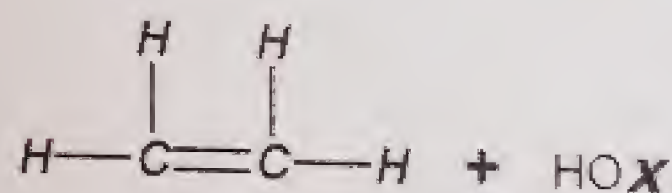
**11. What is nucleophilic reagent?**

An electron rich reagent is called a nucleophilic reagent. e.g.  $\text{NH}_3$ ,  $\text{H}_2\text{O}$  etc.

**12. What is halohydration?**

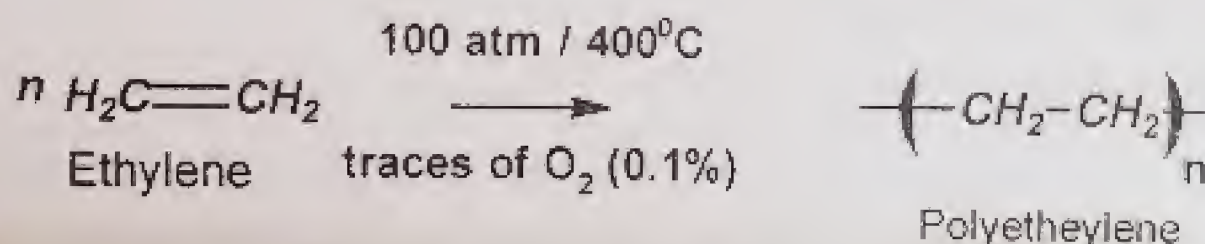
Addition of hypohalous acid ( $\text{HOX}$ ) is called halohydration.

Alkenes react with hypohalous acid to give Halohydrin. In this reaction, molecules of the solvent become reactants too.



**13. What is polymerization**

- Polymerization is a process in which a small organic molecules which are called monomers combine together to form larger molecules. The substances so produced are called polymers.
- Ethene polymerizes to polythene at  $400^\circ\text{C}$  at a pressure of 100 atm.



**Exercise Q3(1).** What is isomerism? Explain different types of isomerism?

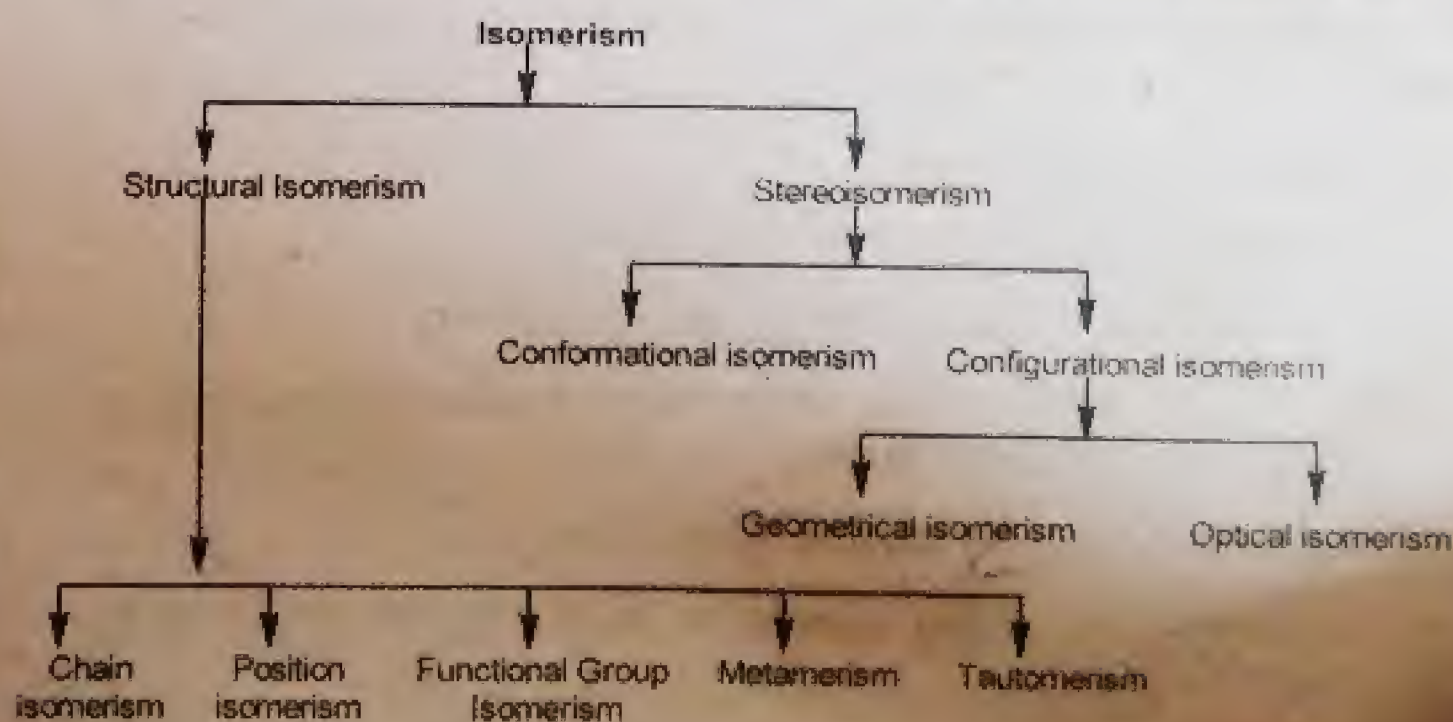
**ISOMERISM**

Compounds that have the same molecular formula but different chemical structures are called isomers and the phenomenon is called isomerism.

The difference in properties of isomers must be due to different modes of combination or arrangement of atoms within the molecule.

**Configuration:**

The term configuration is the three-dimensional arrangement of atoms that characterizes a particular compound.





There are two main types of isomerism:

- (1) Structural Isomerism
- (2) Stereoisomerism

## STRUCTURAL ISOMERISM

When the isomerism is due to difference in the arrangement of atoms within the molecule, without any reference to space, the phenomenon is called **Structural Isomerism**.

Structural isomers are compounds that have the same molecular formula but different structural formulas.

Structural isomerism is of five types:

1. (a) Chain isomerism
2. (b) Position isomerism
3. (c) Functional isomerism
4. (d) Metamerism
5. (e) Tautomerism

## STEREISOMERISM

When isomerism is caused by the different arrangements of atoms or groups in space, the phenomenon is called **Stereoisomerism**.

- The stereoisomers have the same structural formulas but differ in arrangement of atoms in space.
- Stereoisomer is exhibited by such compounds which have the same structural formula but differ in configuration.

Two important types of stereoisomerism are:

- (a) Geometrical or cis-trans Isomerism
- (b) Optical Isomerism

## CHIRAL CENTER

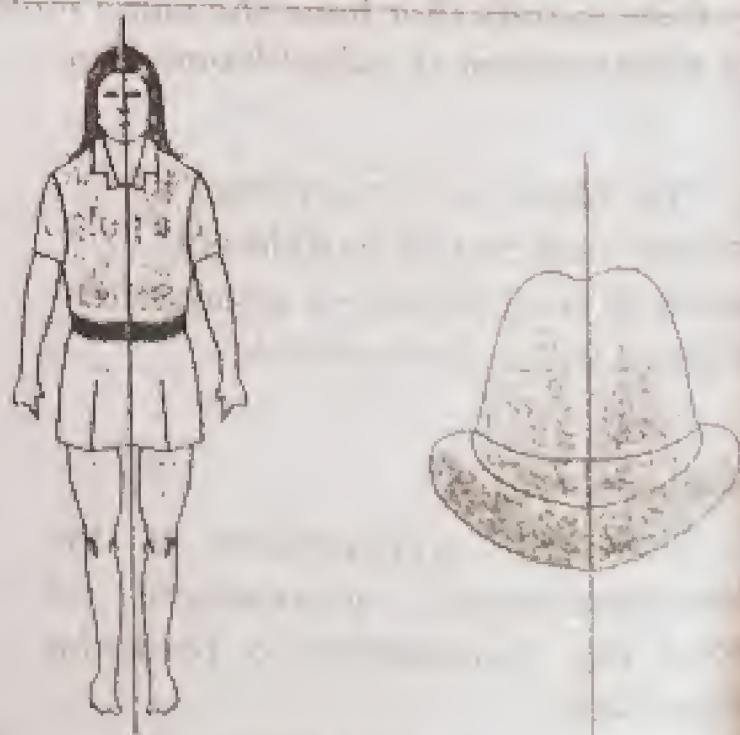
The center in a molecule due to which molecule becomes asymmetric is called a **chiral center**.

## PLANE OF SYMMETRY

A plane which divides an object into two symmetrical halves, is said to be **plane of symmetry**.

**Examples and Explanation:**

- A person or a hat has a plane of symmetry.
- A person's hand or gloves lack plane of symmetry.
- An object lacking a plane of symmetry is called **dissymmetric** or **Chiral** (pronounced as Ki-tal).
- A symmetric object is referred to as **Achiral**.
- A dissymmetric object cannot be superimposed on its mirror image.



Planes of Symmetry



e.g. A left hand does not possess a plane of symmetry. So, its mirror image is not another left hand but a right hand. Both hands cannot be superimposed on each other. If we were to lay one hand on top of the other, the fingers and the thumb would clash.

The mirror image relationship of the left and right hands is shown in the figure. It should be noted that right hand is the mirror image of the left hand.



**Chiral molecule** has at least one asymmetric center and does not have a plane of symmetry.



Chiral objects

- An **achiral molecule** has a plane of symmetry.

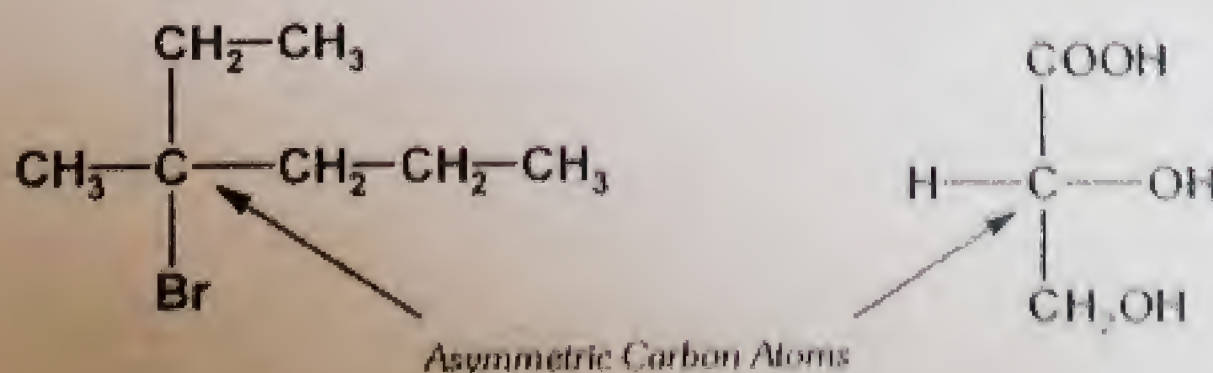


Achiral objects

### CARBON-BASED CHIRAL CENTERS:

A carbon atom which is bonded to four different groups is called an Asymmetric Carbon Atom or Chiral Carbon Atom.

Examples:



- The term asymmetric carbon atom is misleading. It only means that a carbon atom is bonded to four different groups. Such type of molecule lacks plane of symmetry and is called asymmetric (Latin a = without), that is, without symmetry.
- Presently the term Dissymmetric or Chiral Molecules is often used for asymmetric molecules.



## OPTICAL ACTIVITY

A substance that can rotate plane of polarized light is called optically active and this property of a substance is called optical activity.

### Explanation

- Electromagnetic light vibrates in all possible planes. When this light is passed through a Nicol prism (made of calcite,  $\text{CaCO}_3$ ) or Polaroid lens, it allows only those radiation to pass through it, which are parallel to its axis. This light vibrating only in one plane is called plane polarized light or simply polarized.
- When plane polarized light will pass through a solution of an optically active compound, the compound will rotate the plane polarized light either to left or right. These compounds are said to be Optically Active. This property of a compound is called Optical Activity.

### Dextrorotatory Compound

The compound, which rotates the plane of polarized light towards right (clock-wise), is called a dextrorotatory compound. It is indicated by the sign (+) sign.

### Levorotatory Compound

The compound, which rotates the plane of polarized light towards left (anticlock-wise), is called a levorotatory compound. It is indicated by the sign (-) sign.

### Measurement of Optical Rotation

The instrument used to measure direction and magnitude of optical rotation is called Polarimeter.

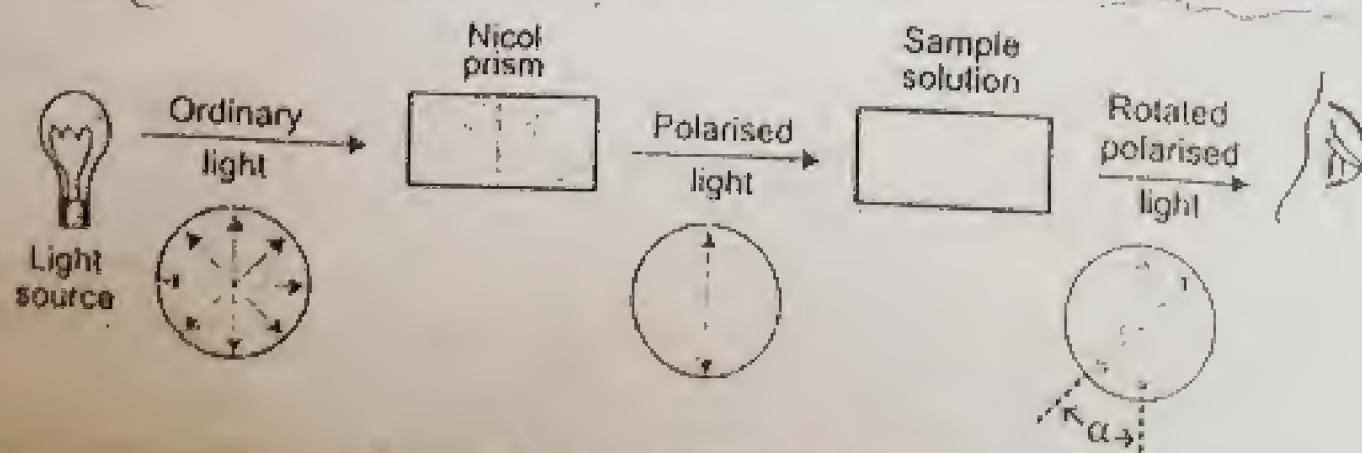
### Construction

It has following basic parts

- Fixed polarizer (Nicol prism) to polarize light
- Movable analyzer (Nicol prism).
- A tube containing test solution placed between polarizer and analyzer
- A light source.

### Working

- Light from light source passes through polarizer and is polarized. If the sample tube is empty, then parallel position of polarizer and analyzer gives maximum illumination. This is the zero reading.
- Now a solution of known concentration of an optically active compound is placed in the sample tube. The solution will rotate the plane polarized light through a certain number of degrees. Thus less light will pass through analyzer and there will be less illumination.
- In order to get maximum illumination again, analyzer is rotated, the angle through which analyzer is rotated gives the magnitude of observed rotation ( $\alpha$ ).
  - If rotation is to the right, it is said to be (+) and the compound is called dextrorotatory.
  - If rotation is to the left, it is said to be (-) and the compound is called levorotatory.



A simple polarimeter in operation



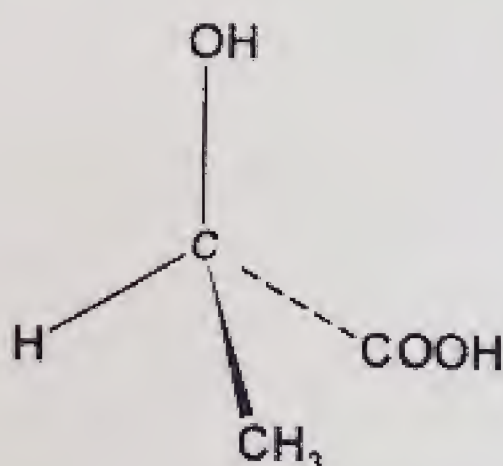
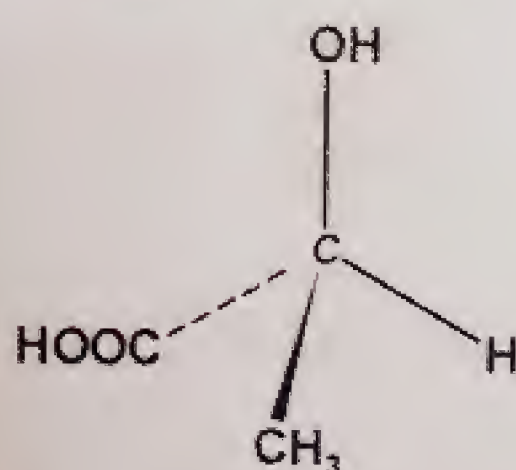
## STEREISOMERISM: OPTICAL ISOMERISM

An optically active compound can exist in two isomeric forms which rotate the plane polarized light in opposite directions. These are called Optical Isomers and the phenomenon is known as Optical Isomerism.

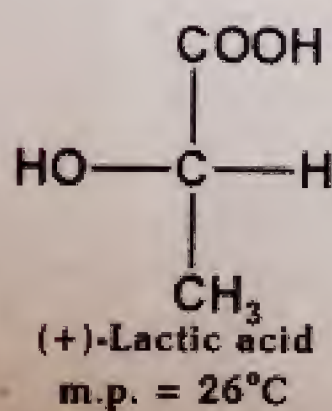
- The isomer which rotates the plane of polarized light to the right (clockwise direction) is known as **Dextrorotatory** Isomer or (+) isomer.
- The isomer which rotates the plane of polarized light to the left (anticlockwise direction) is known as the **Laevorotatory** Isomer or (-) isomer.

### Optical Isomerism of Lactic Acid

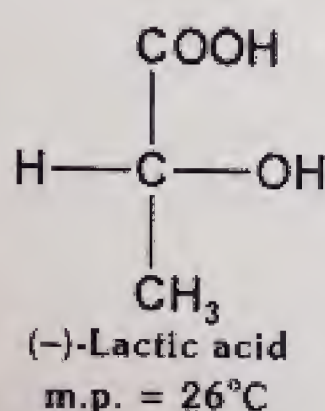
- Lactic acid (2-Hydroxypropionic acid) is an example of a compound which shows optical isomerism. It contains one asymmetric carbon atom.
- Two three dimensional structures are possible for Lactic acid



Mirror



(I)



(II)

Equimolar mixture of (+) and (-) forms is called racemic mixture. It is denoted as  $(\pm)$ .

e.g.  $(\pm)$ -Lactic acid

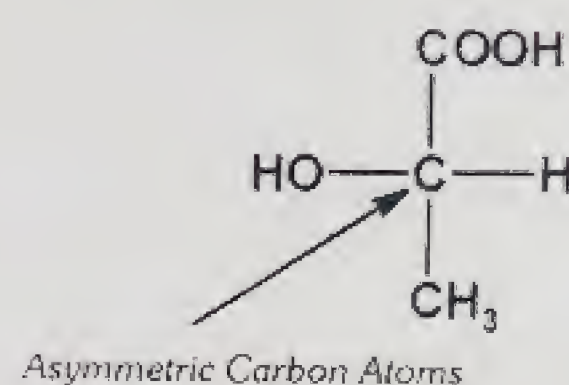
(III)

- These structures are not identical because they cannot be superimposed on each other.
- The non-superimposable mirror images of each other are called **Enantiomers**.
- Equimolar mixture of two enantiomers is called racemic mixture. It is optically inactive and denoted by  $(\pm)$ .
- Thus, three forms of lactic acid are known. Two are optically active and one is optically inactive.

**(+)-Lactic Acid:** It rotates the plane of polarized light to the right (clockwise direction) is called **dextrorotatory**.

**(-)-Lactic Acid:** It rotates the plane of polarized light to the left (anticlockwise direction) is called **laevorotatory**.  
(-)-Lactic acid is the mirror image of (+)-lactic acid and vice versa.

**$(\pm)$ -Lactic Acid:** It does not rotate the plane of polarized light. That is, it is optically inactive. It is an equimolar mixture of (+) and (-) forms. It is called **racemic mixture**.



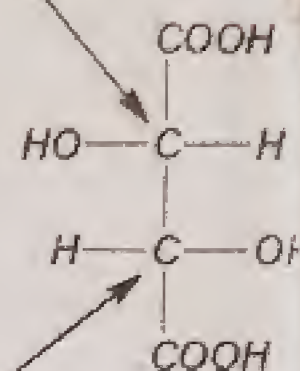


## Optical Isomerism of Tartaric Acid

Tartaric acid (2,3-Dihydroxybutanedioic acid) contains two asymmetric carbon atoms.

- Four forms of tartaric acid are known.
- Two of them are optically active and two are optically inactive.
- The optically active forms are related to each other as a non-superimposable mirror image of each other. They are enantiomers.

Asymmetric Carbon Atom



Asymmetric Carbon Atom

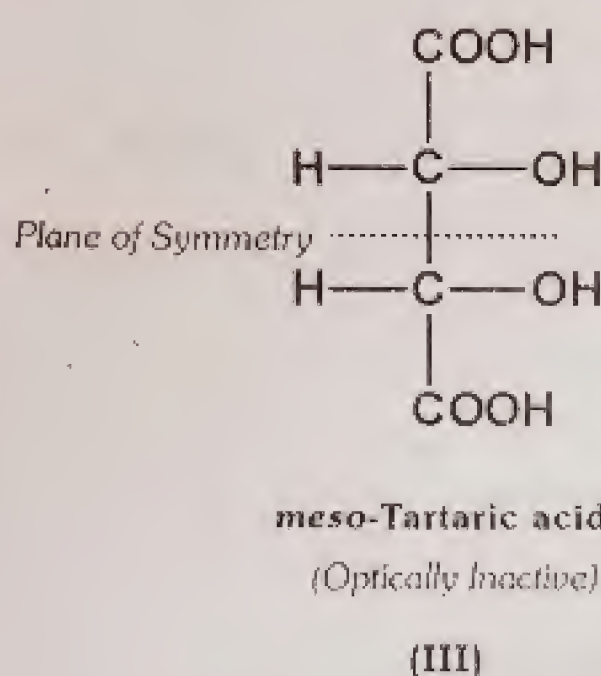
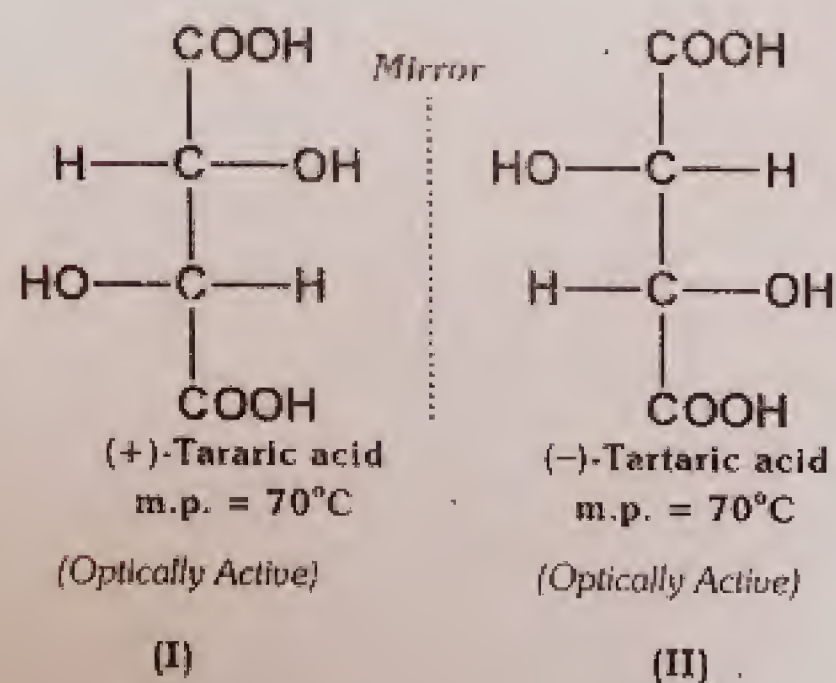
Two Asymmetric Carbon Atoms in Tartaric acid

**(+)-Tartaric Acid:** It rotates the plane of polarized light to the left (anticlockwise direction) is called laevorotatory. (-) Lactic acid is the mirror image of (+) lactic acid and vice versa.

**(-)-Tartaric Acid:** It rotates the plane of polarized light to the right (clockwise direction) is called dextrorotatory.

**(±)-Tartaric Acid:** It does not rotate the plane of polarized light. Thus, it is optically inactive. It is an equimolar mixture of (+) and (-) forms (racemic mixture).

**meso-Tartaric Acid:** It has plane of symmetry. So, it does not rotate the plane of polarized light. Thus, it is optically inactive.



Equimolar mixture of (+) and (-) forms is called racemic mixture. It is denoted as (±)

e.g. (±)-Tartaric acid  
(Optically Inactive)

(IV)

Isomers of Tartaric Acid

### Important!

- In isomers of tartaric acid, (I) and (II) are enantiomers.
- However, (I) and (III) are called diastereomers. They are not mirror image of each other.
- Similarly, (II) and (III) are also diastereomers.

### Diastereomers

**Stereoisomers of the same compound which are not mirror image of each other are called diastereomers.** Although enantiomers have same physical properties like melting points etc. The diastereomers are totally different compounds with different physical properties.



## ISOMERISM - GEOMETRIC ISOMERISM

Geometrical isomerism (also called cis-trans isomerism) results from a restriction in rotation about double or about single bonds in cyclic compounds.

### GEOMETRICAL ISOMERISM IN ALKENES

The carbon atoms of the carbon-carbon double bond are  $sp^2$ -hybridized.

The carbon-carbon double bond consists of a sigma bond and a pi bond.

The sigma bond is formed by the overlap of  $sp^2$  hybrid orbitals.

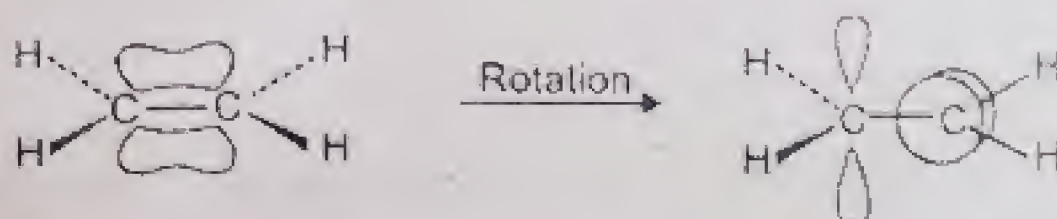
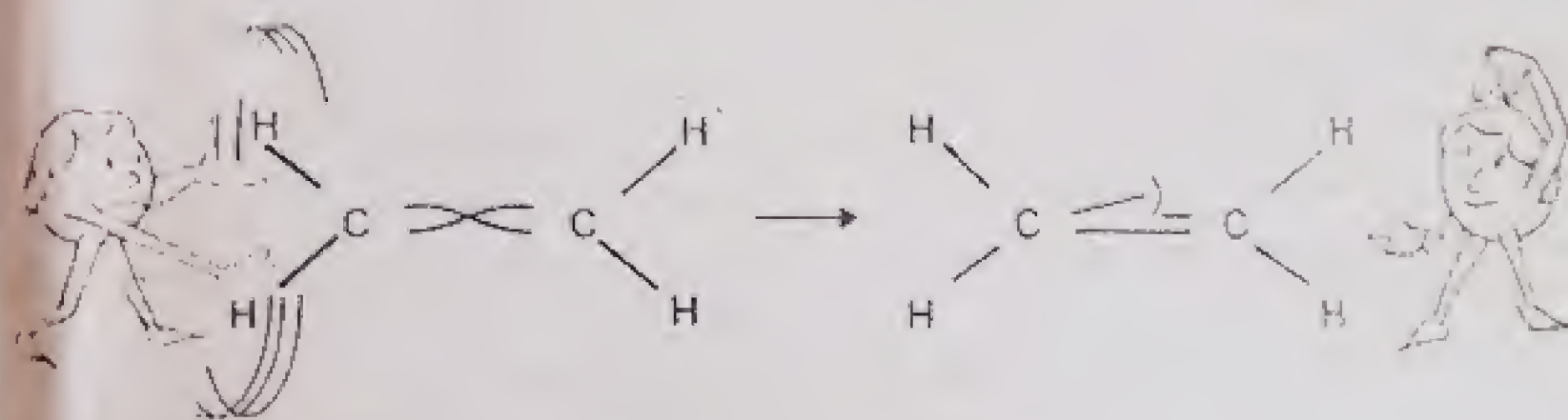
The pi bond is formed by the overlap of p orbitals.

The presence of the pi bond locks the molecule in one position.

The two carbon atoms of the  $C=C$  bond and the four atoms that are attached to them lie in one plane and their position in space are fixed.

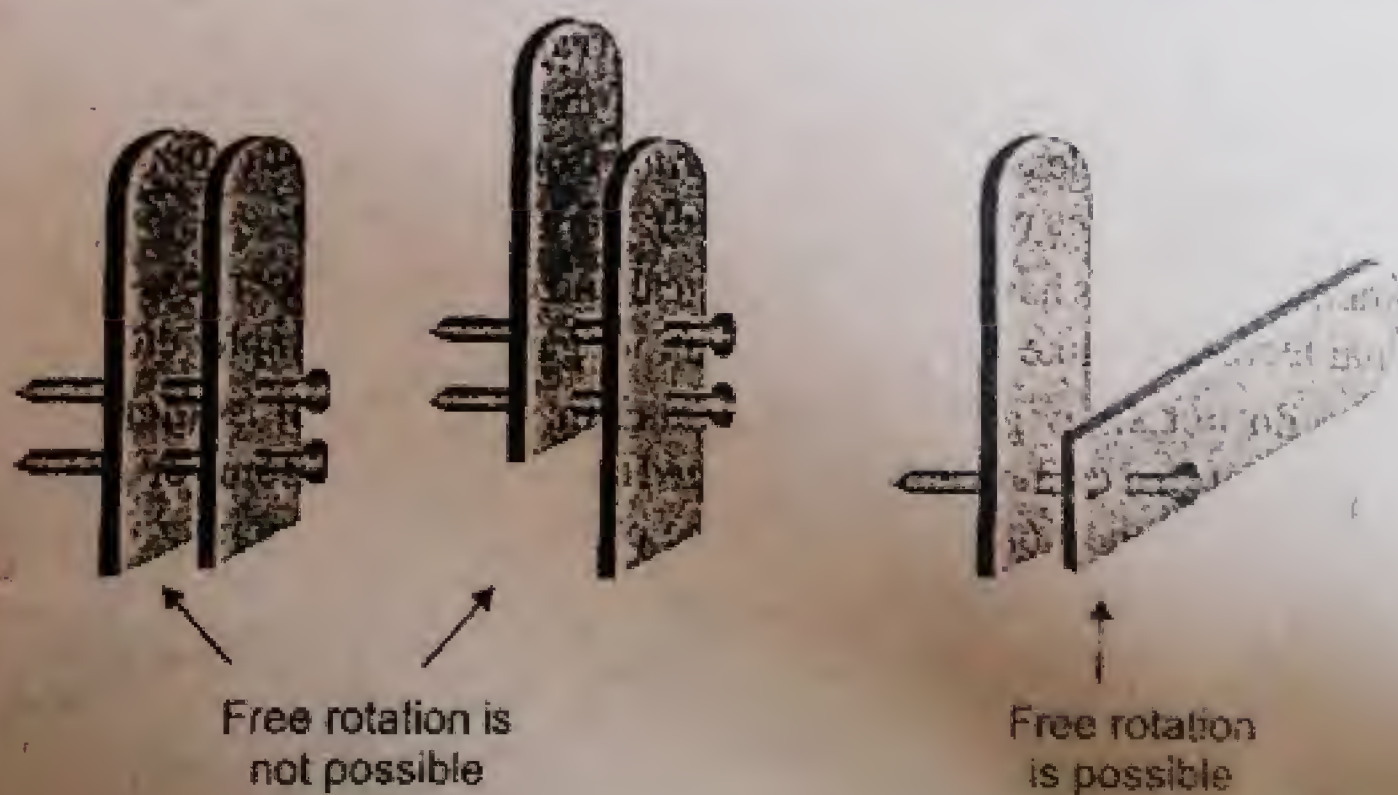
Rotation around the  $C=C$  bond is not possible because rotation would break the pi bond.

The restriction of rotation about the carbon-carbon double bond is responsible for the geometrical isomerism in alkenes.



Rotation about pi bond is not possible because it would break the pi bond

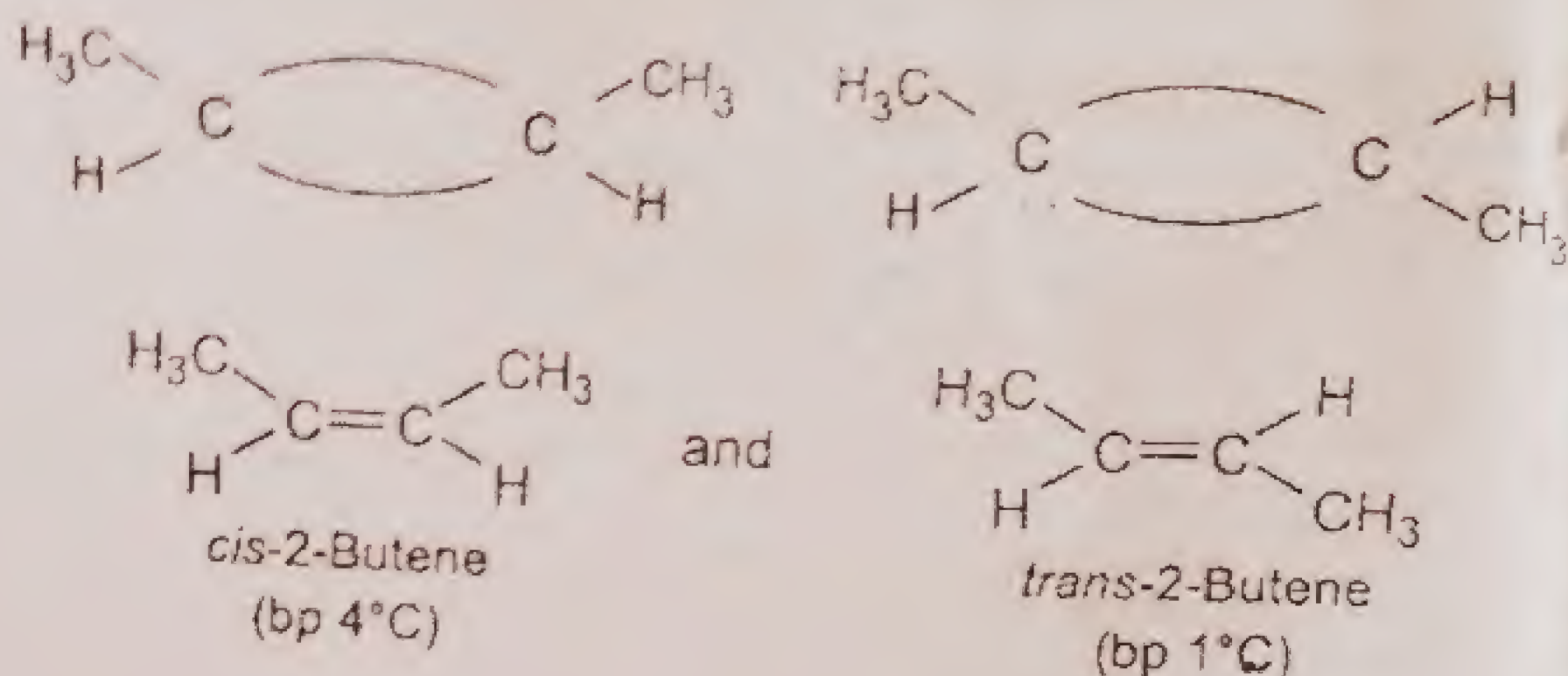
A similarity for this situation is based upon two boards and two nail. Driving one nail through two boards, will not prevent free rotation of the two boards. But once a second nail is used, the boards cannot be freely rotated.





**Example:**

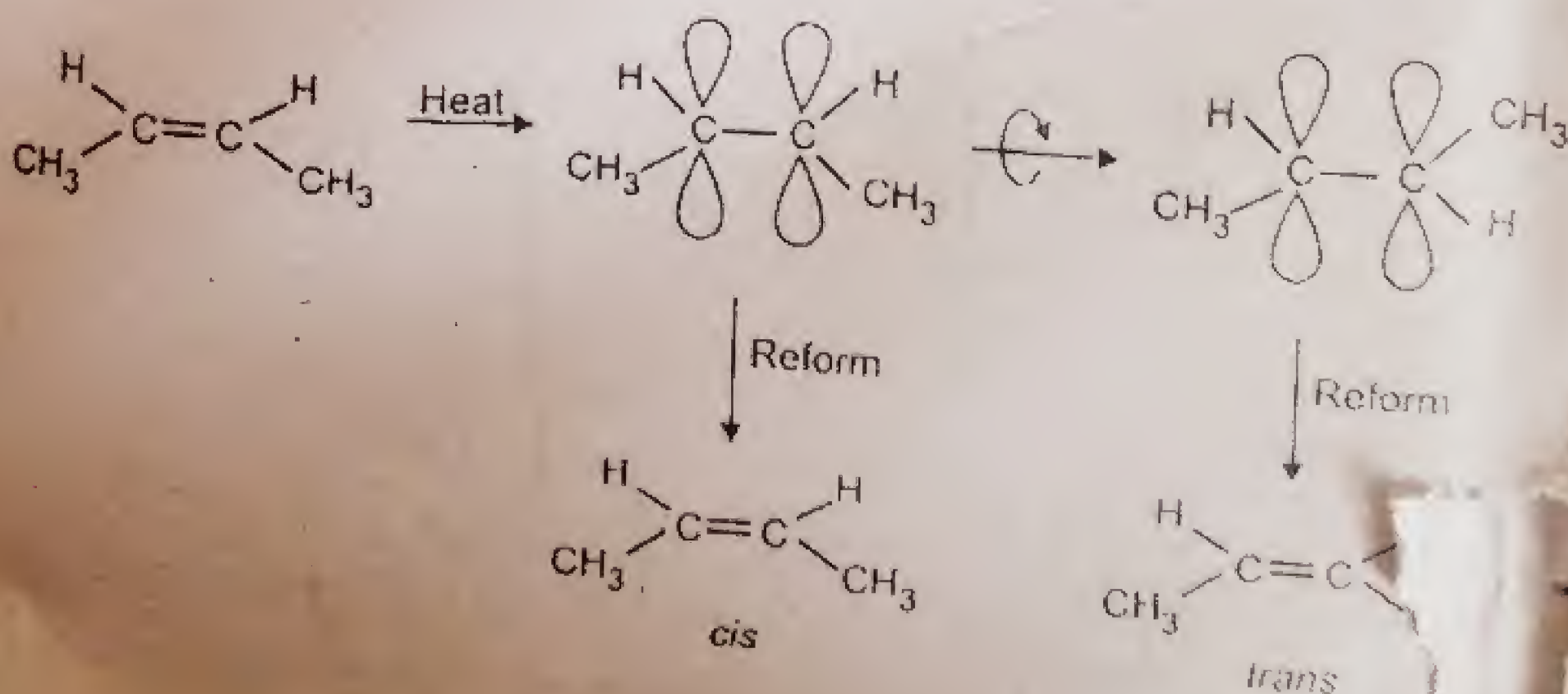
- Consider the case of 2-butene. It exists in two spatial arrangements:



- These two compounds are called as geometrical isomers. These are named as cis and trans. Hence, this type of isomerism is also called cis-trans isomerism.
- ✓ The cis isomer is one in which two similar groups are on the same side of the double bond.
- ✓ The trans isomer is that in which two similar groups are on the opposite sides of double bond.
- Geometrical isomers are stereoisomer, because they have the same structural formula but different arrangement of atoms.
- The geometrical isomers have different physical and chemical properties.
- They can be separated by conventional isomers have different physical techniques like fractional distillation, gas chromatography etc.

**Inter-Conversion of cis-, trans-Isomers**

- The conversion of cis-isomer into trans-isomer or vice versa is possible only if either isomer is heated to high temperature or absorbs light.
- The heat supplies the energy (about 62 Kcal/mole) to break the pi-bond so that rotation about sigma bond becomes possible.
- Upon cooling, the reformation of the pi bond can take place in two way giving mixture of trans-2-butene plus cis-2-butene.





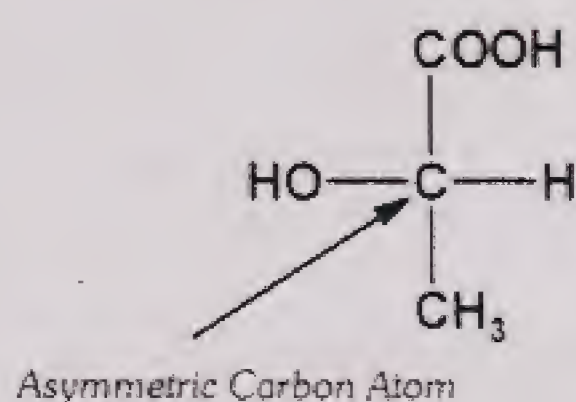
## QUICK QUIZ-4

Define or explain the following terms

- (a) Structural isomerism      Page 165  
 (b) Stereoisomerisms      Page 156, 159  
 (c) Geometrical isomerism      Page 161  
 (d) Optical isomerism      Page 159  
 (e) Asymmetric carbon

A carbon atom to which four different groups are attached is called an asymmetric carbon.

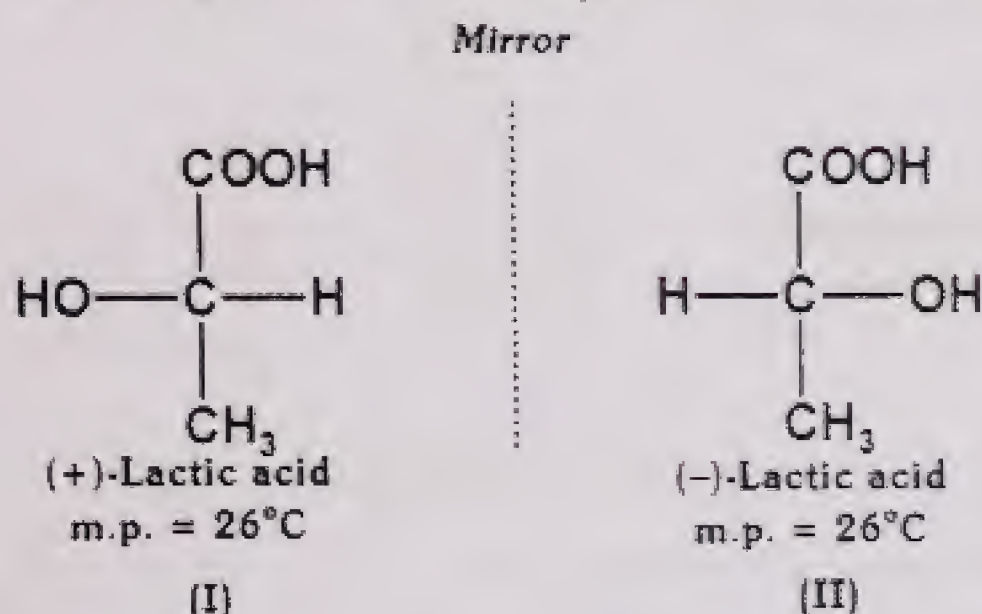
Example:



(f) Chiral molecule

A molecule which has non-superimposable mirror image is called a chiral molecule.

Example: Lactic acid



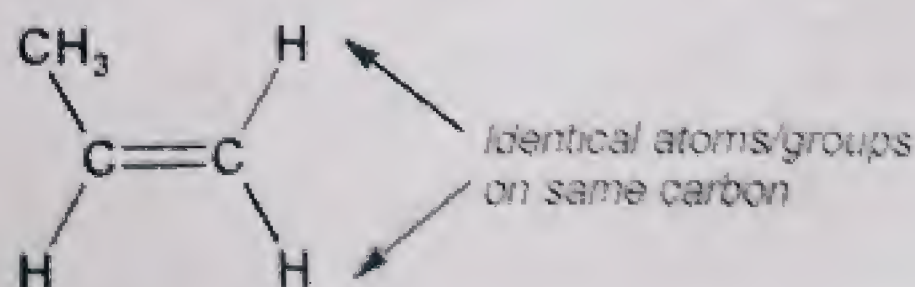
2. State the necessary condition for a compound to show geometrical isomerism. Illustrate your answer with examples

Conditions of Geometrical Isomerism

- (i) Presence of double bond or cyclic ring  
 (ii) Two different groups must be attached, to each carbon of double bond, or to different carbons of cyclic ring.

Example 1.

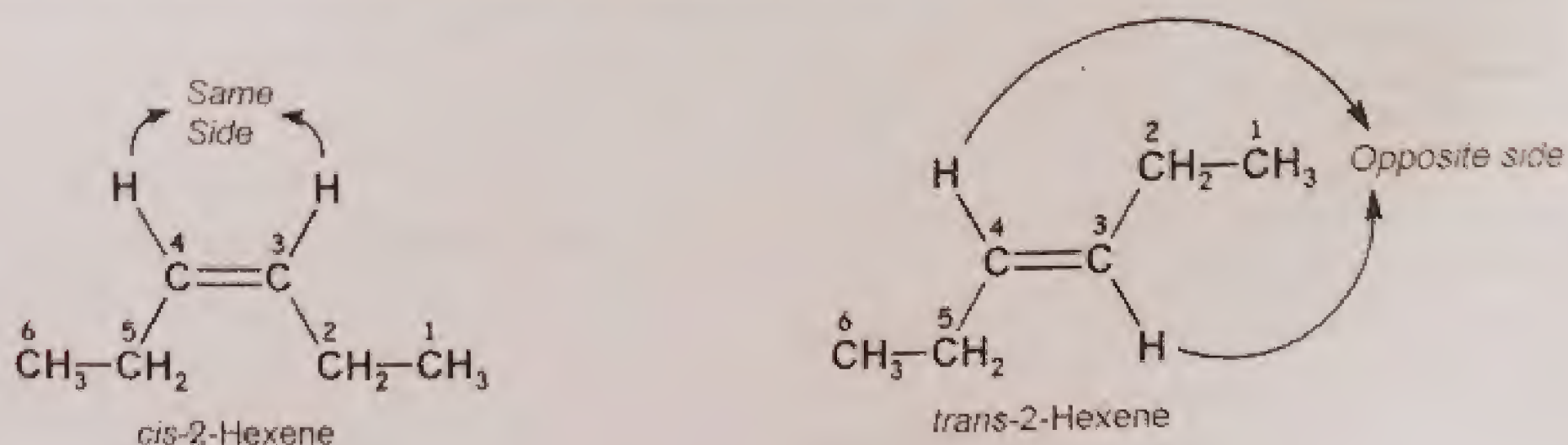
No geometrical isomers are possible for propene. It is because one of double bonded carbons has two identical groups (H atoms) attached to it.





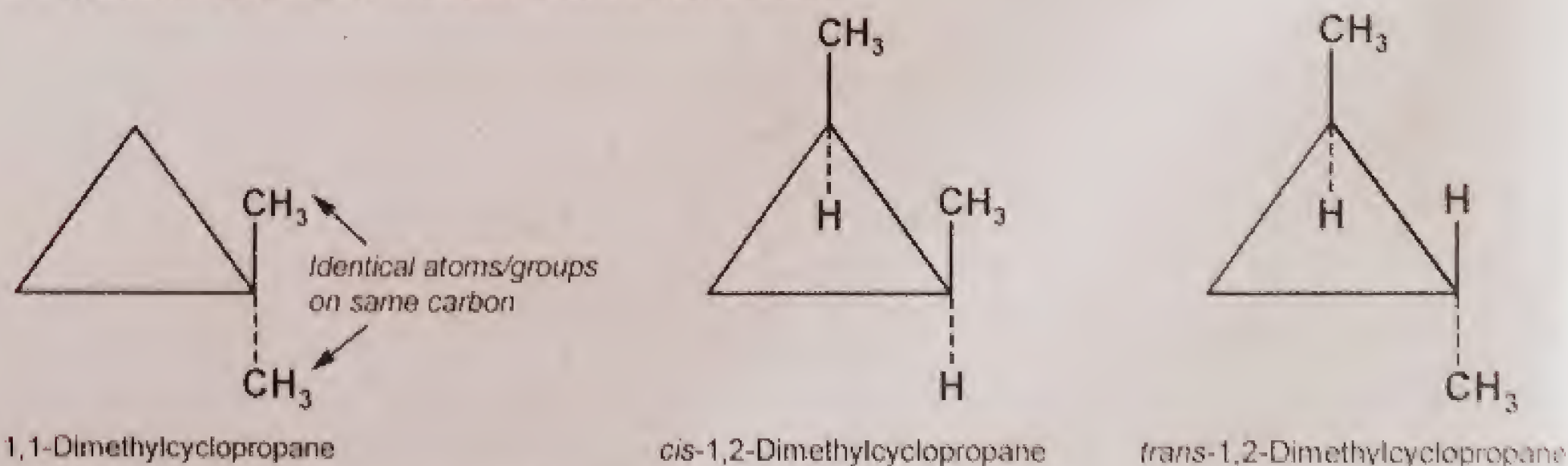
**Example 2.**

Geometrical isomers are possible for 3-hexene ( $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$ ). This is because each double bond carbon atom is attached to two different groups ( $\text{CH}_3\text{CH}_2$  and  $\text{H}$ ).



**Example 3.**

- No geometrical isomers are possible for 1,1-dimethylcyclopropane.
- 1,2-dimethylcyclopropane exists in two isomeric forms.

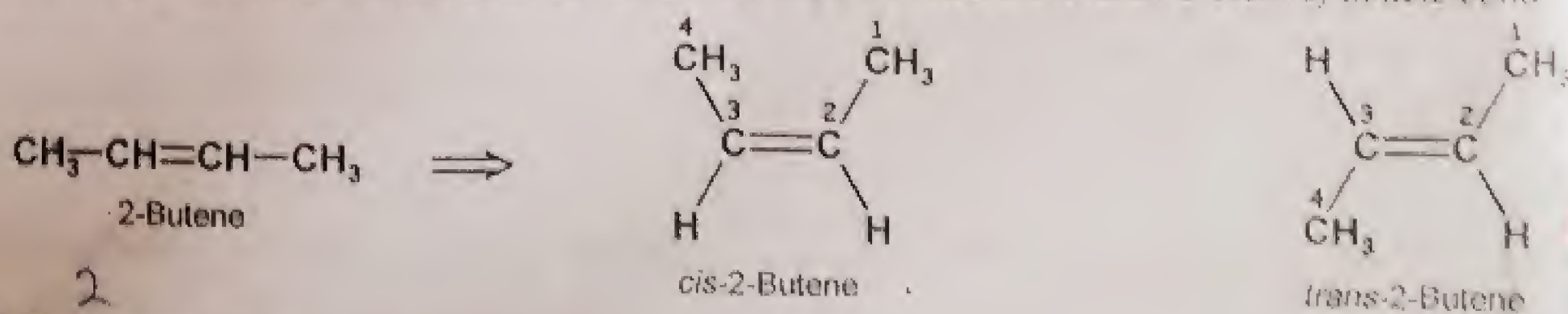


- In *cis*-1,2-dimethylcyclopropane the two methyl groups are on the same side of ring.
- In *trans* 1,2-dimethylcyclopropane, they are on opposite sides.

**3. Which of the following compounds shows geometrical isomerism?**

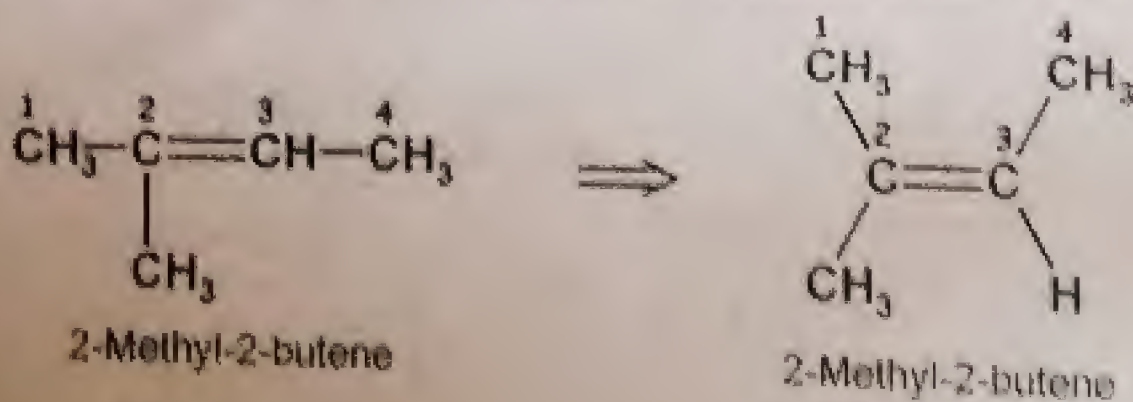
**(a) 2-Butene**

It will show geometrical isomerism since two different groups are attached to each C atom of double bond



**(b) 2-Methyl-Butene**

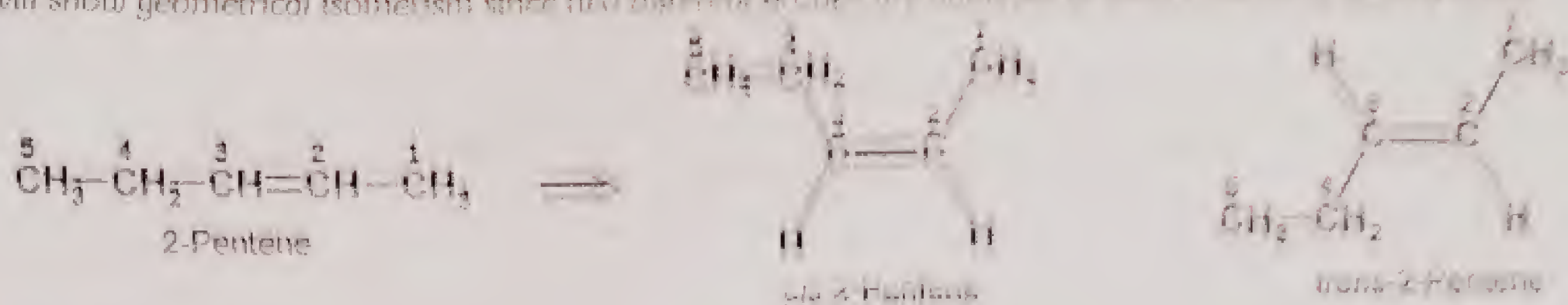
It will not show geometrical isomerism since one carbon of double bond has two same groups attached to it





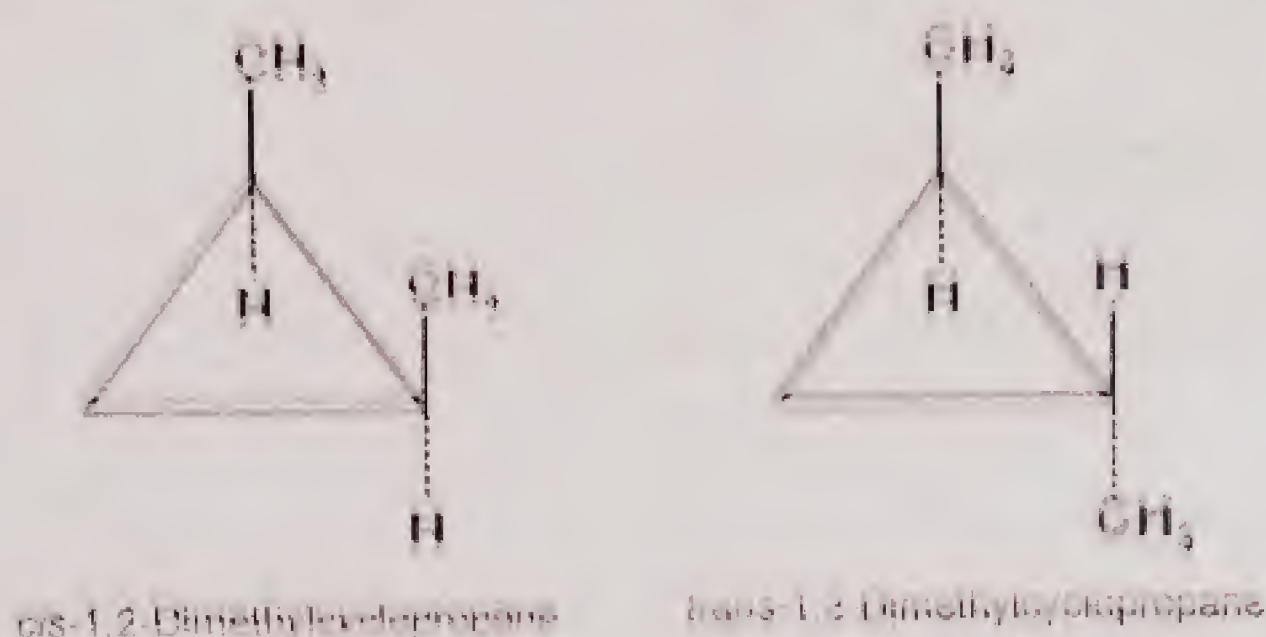
(c) **2-Pentene**

It will show geometrical isomerism since two different groups are attached to each C atom of double bond



(d) **1,2-Dichloropropane**

It will show geometrical isomerism since two different groups are attached to two different carbon atoms of cyclic ring.



4. Which of the following compounds show isomerism?

(a) **CH<sub>2</sub>-CH=CH<sub>2</sub>**

- It will not show geometrical isomerism (one carbon of double bond has two hydrogens (identical groups) attached to it)
- It will not show optical isomerism (since it does not have any chiral carbon).

**NOTE:** It will show structural isomerism with cyclopropane. Both have same molecular formula (C<sub>3</sub>H<sub>4</sub>) but different structures and properties. Both are *chain isomers* of each other.



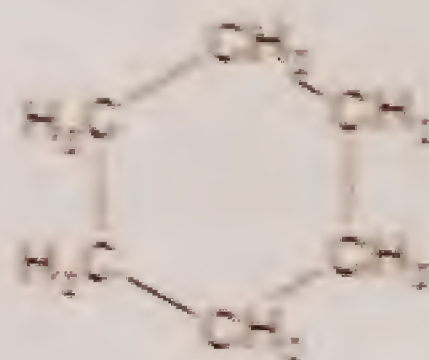
(b) **CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CHCH<sub>3</sub>**

- It will not show optical isomerism (since it does not have any chiral carbon)
- It will show geometrical isomerism (since two different groups are attached to each C atom of double bond)





**NOTE:** It will show structural isomerism with cyclohexane. Both have same molecular formulae different structures and properties. Both are chain isomers of each other.



5. What is optical activity: how is it measured?

Page 158

6. Write a note on Optical Isomerism of Lactic acid

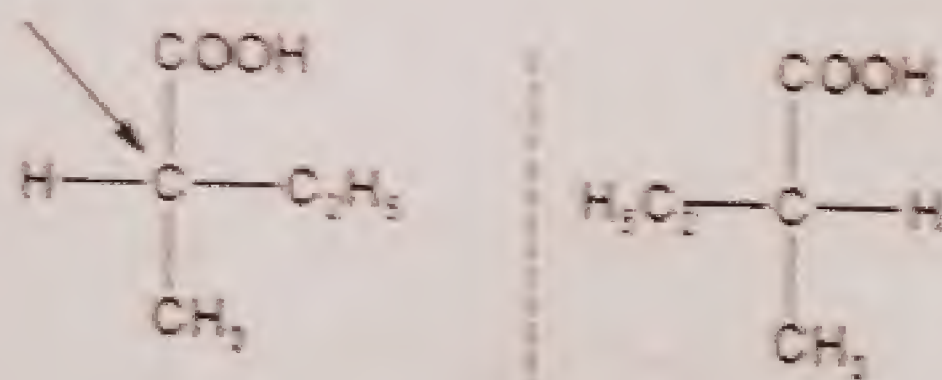
Page 159

7. Write a note on Optical isomerism of tartaric acid

Page 160

8. An acid of formula  $\text{C}_4\text{H}_8\text{O}_2$  is optically active. What is its structure?

Asymmetric carbon



2-Methylbutanoic acid  
(Enantiomers)

9. How does cis-isomer convert into trans-isomer?

Page 162

10. The trans-isomer is more stable. Why?

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# ALKYNES

## I.U.P.A.C. NOMENCLATURE

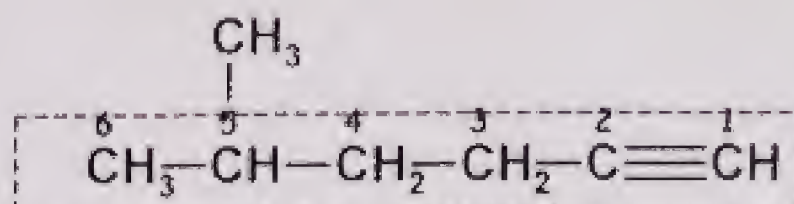
- (1) The parent hydrocarbon is the continuous chain containing triple bond.
- (2) The ending 'ane' of the alkane is changed by **-yne**.



Ethyne

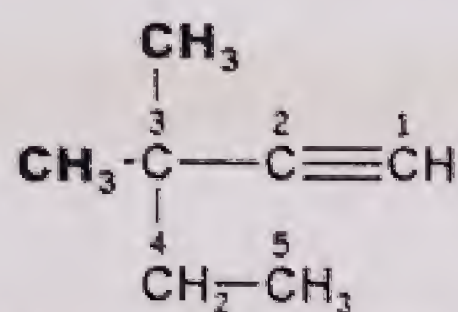


Propyne



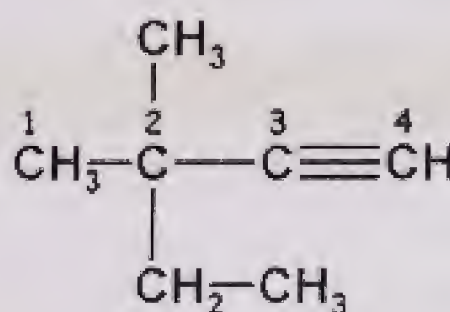
5-Methyl-1-hexyne

- (3) The main chain is numbered starting from the terminal carbon nearer to the triple bond.



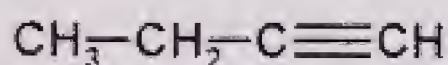
3,3-Dimethyl-1-pentyne

(Correct)



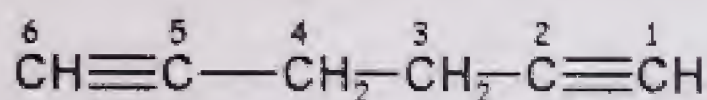
(Incorrect)

- (4) Triple bond is given the number of the lower carbon atom attached to triple bond separated by hyphen.



1-Butyne

- (5) If two or more triple bonds are there in the molecule, use the prefixes di-, tri-, etc.

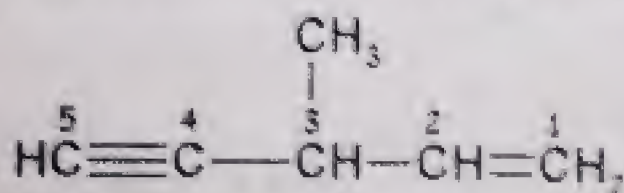


1,5-Hexadiyne

- (6) Alkyl groups are indicated by the methods described while naming alkanes.

## NAMING OF MOLECULES CONTAINING BOTH THE DOUBLE AND TRIPLE BONDS

- (1) The suffix 'ene' is used to denote the presence of Double bond
- (2) the suffix **-yne** to denote the presence of triple bond.
- (3) The suffix **-ene** always precedes **-yne** in the name of compound, even when the double bond is assigned the large number.
- (4) The position number for the double bond is placed before the name of parent hydrocarbon.
- (5) The position number of triple bond is placed between **-ene** and **-yne**.
- (6) If **same** number would result from each terminal, the double bond is given the lower possible number e.g.

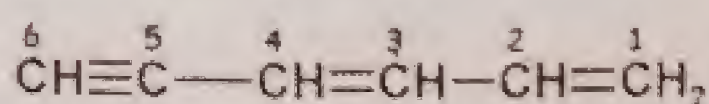


3-Methyl-1-penten-4-yne

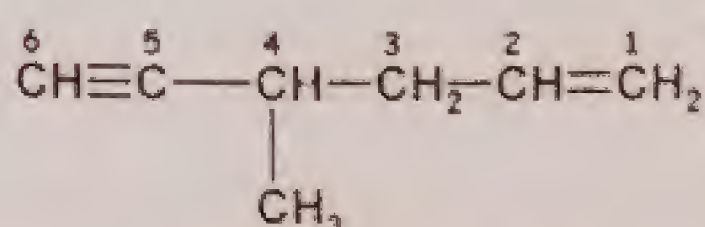




1-Hexen-5-yne



1,3-Hexadien-5-yne



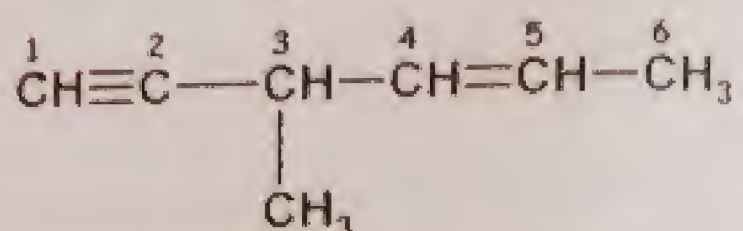
4-Methyl-1-hexen-5-yne



4-Hexen-1-yne



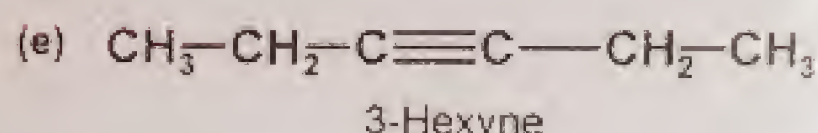
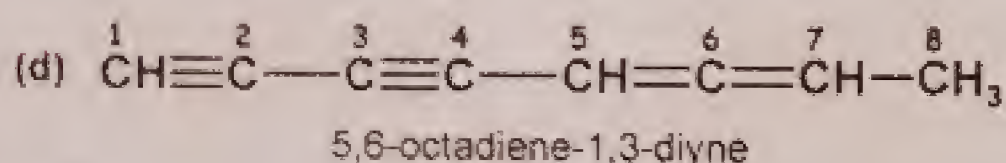
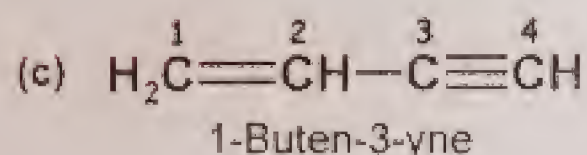
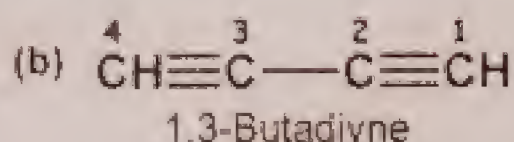
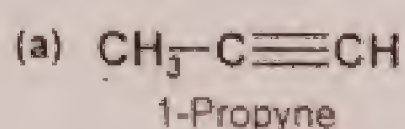
1-Hexene-3,5-diyne



3-Methyl-4-hexen-1-yne

## ACTIVITY

Give the IUPAC name of the following:



## RELATIVE STABILITY

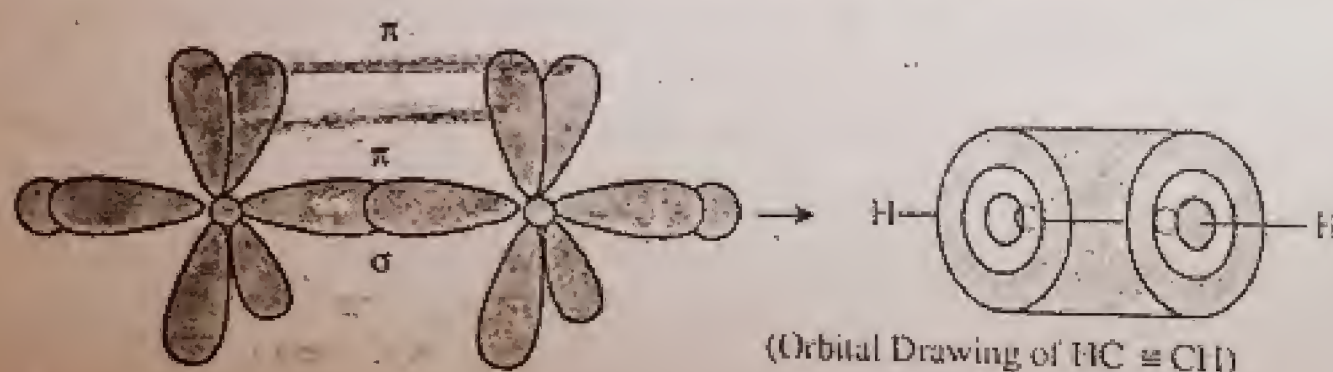
Alkynes are more stable as compared to alkenes due to the presence of extra pi-bond. That is why alkynes are less reactive than alkene.

This can be supported by the thermodynamic data of alkynes and alkenes, i.e.

$\Delta H$  of 1-Hexyne = 290 kJ/mol while  $\Delta H$  of 1-Hexene = 126 kJ/mol. Thus, alkynes require more energy.

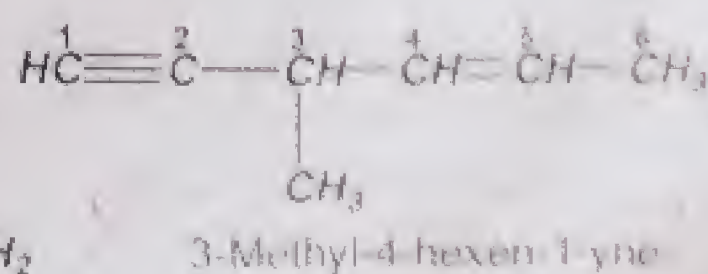
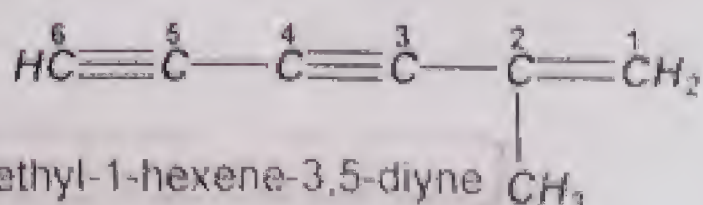
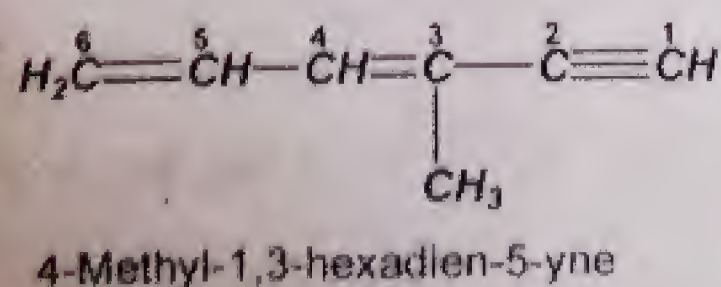
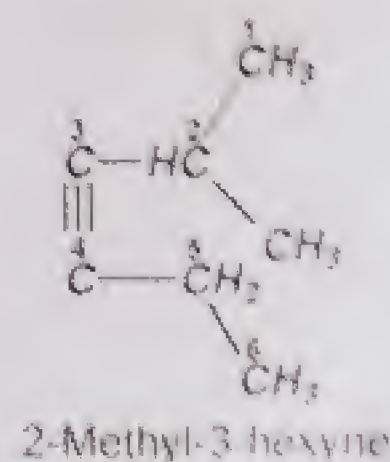
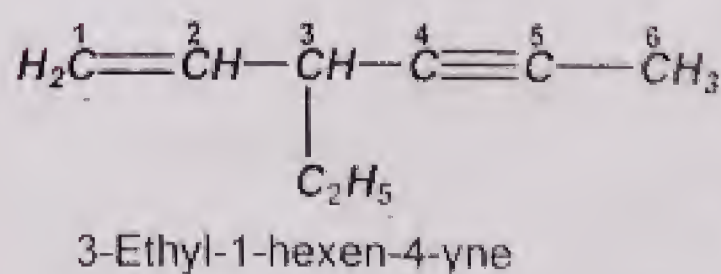
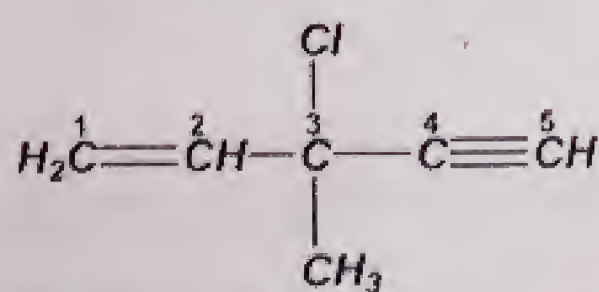
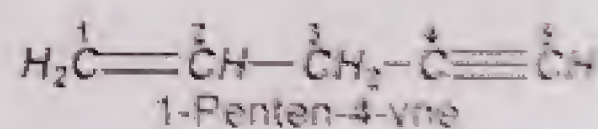
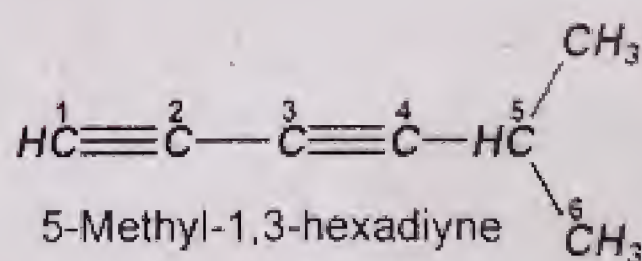
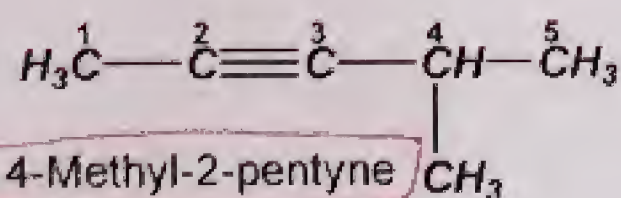
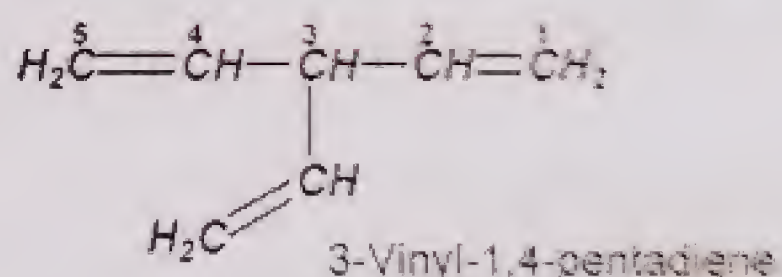
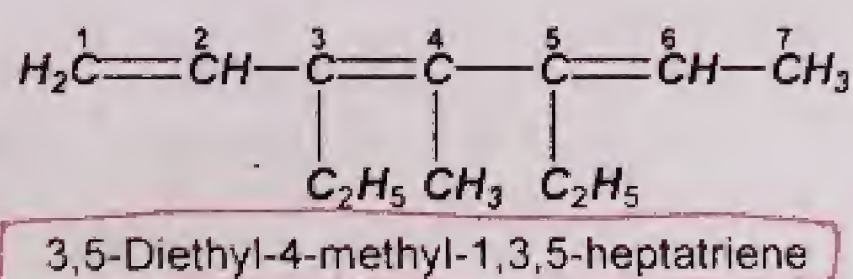
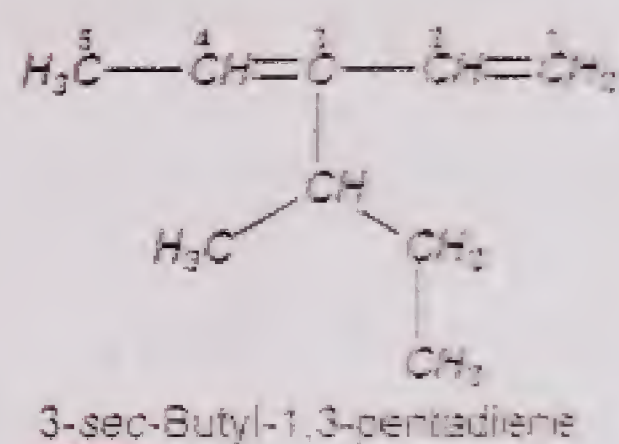
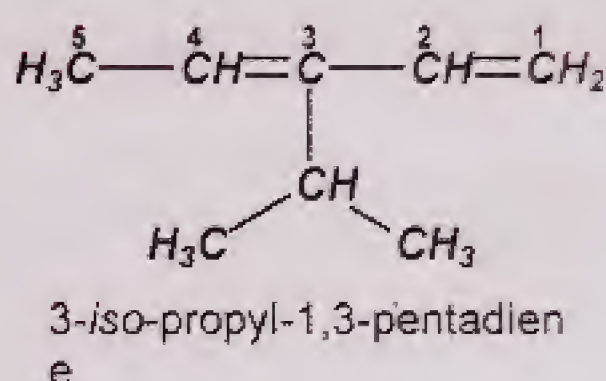
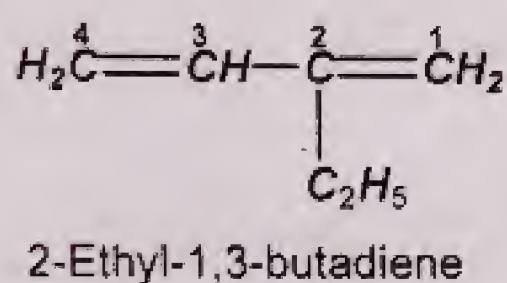
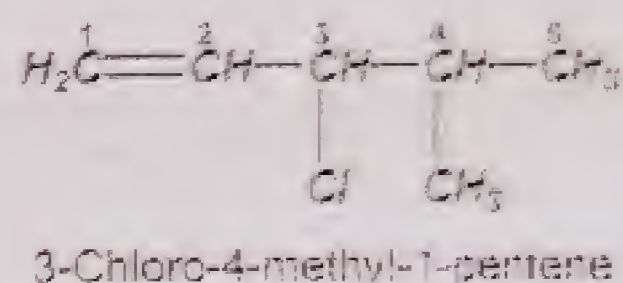
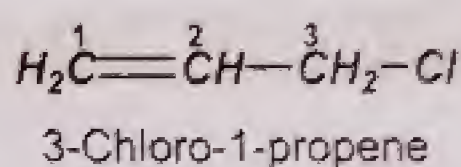
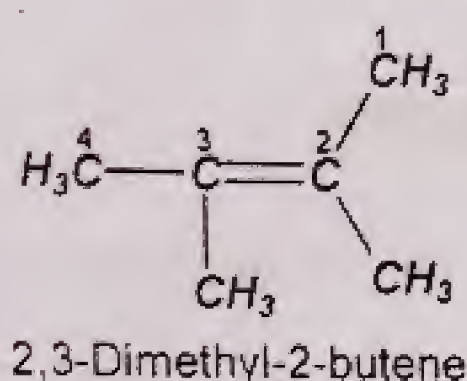
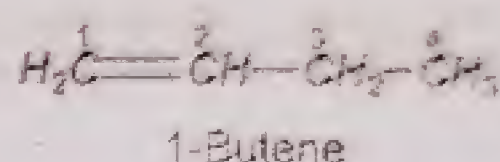
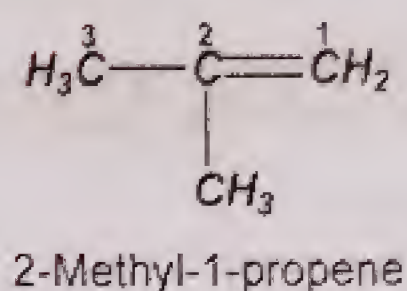
## STRUCTURE

- The two carbons of acetylene (alkyne) are  $sp$ -hybridized. They are linked by a sigma-bond due to  $sp$ - $sp$  orbital overlap.
- The unhybridized two  $p$ -orbitals on one carbon overlap with two  $p$ -orbitals on other carbon to form two pi-bonds.
- The cloud of pi-electrons is present cylindrically symmetrical about the carbon-carbon sigma-bond.



- Rotation about carbon-carbon sigma bond does not cause any change in energy and electron density. It is a linear molecule, and hence geometrical isomer is not observed in it.







## PHYSICAL PROPERTIES

In general, alkynes are non-polar and are insoluble in water but soluble in non-polar organic solvents.

## PREPARATION OF ALKYNES BY ELIMINATION REACTIONS

Alkynes can be prepared by the following methods:

- Elimination reaction
- Alkylation of sodium acetylide.

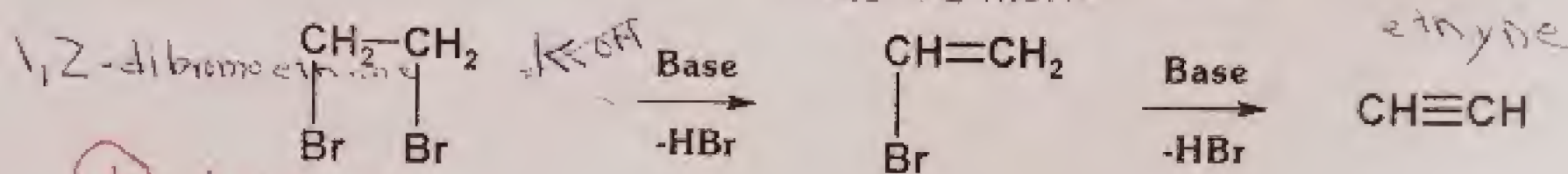
### (i) ELIMINATION OF HYDROGEN HALIDE (DEHYDROHALOGENATION):

The removal of hydrogen and halogen from a molecule is called dehydrohalogenation.

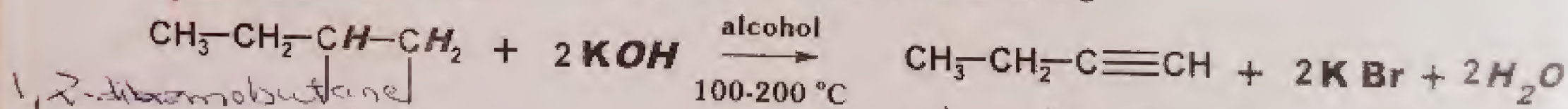
Alkynes can be prepared by dehydrohalogenation of vicinal and geminal dihalides in the presence of some alkaline reagents.

#### (a) Dehydrohalogenation of Vicinal Dihalides

- A vicinal dihalide contains two halogen atoms on adjacent carbon atoms.



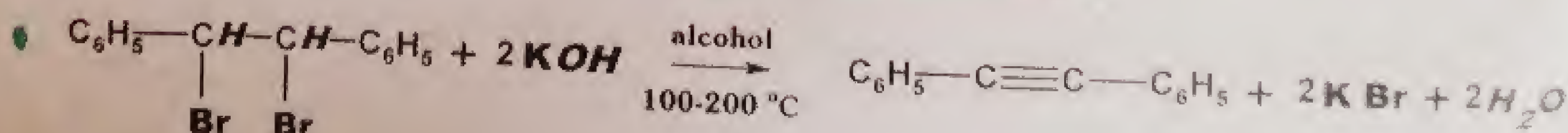
- Higher alkynes are also formed in the presence of alcoholic KOH, e.g.,



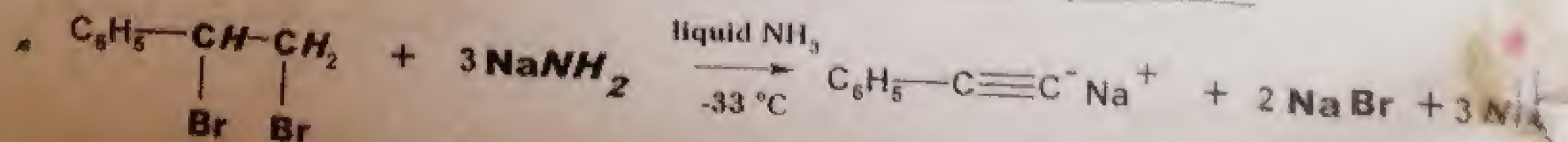
- In the presence of strong base such as KOH and at high temperature triple bond at terminal c-atom migrates to give more disubstituted alkyne.



- Therefore, alcoholic KOH is useful when rearrangement is not possible.



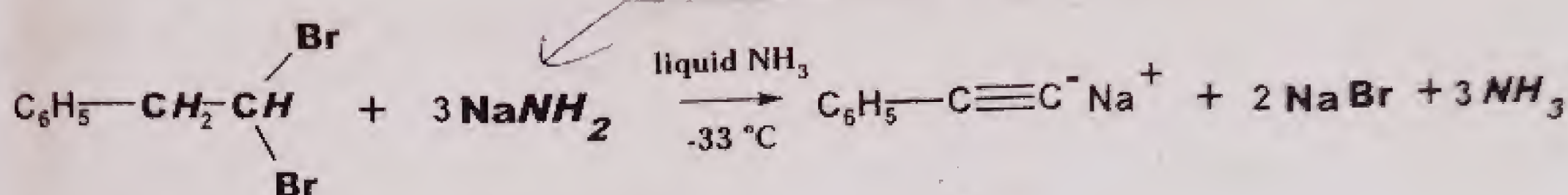
- 1-alkynes can be prepared from vic-dihalides with sodium amide in liquid ammonia.





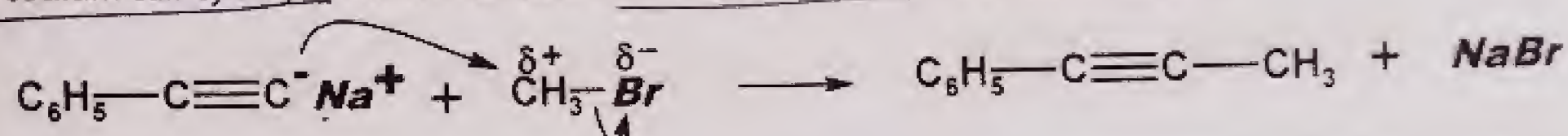
**(a) Dehydrohalogenation of Geminal Dihalides**

A dihalide containing two halogen atoms linked with the same carbon atom) on treatment with strong base gives alkyne, e.g.,



**(ii) ALKYLATION OF SODIUM ACETYLIDE**

The sodium salt of alkyne can be reacted with an alkyl halide to give bigger alkyne.



**REACTIVITY**

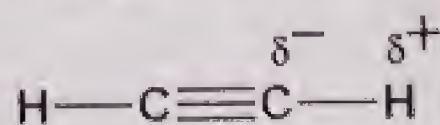
- Acetylene (alkyne) is an unsaturated hydrocarbon and shows addition reactions.
- It also undergoes substitution reactions due to easy cleavage of C-H bond. *Why electrophilic substitution is possible in acetylene*
- The pi-electrons are present cylindrically symmetrical about carbon-carbon sigma bond and the removal of terminal hydrogen is possible without disturbing carbon-carbon bonding. Thus, electrophilic substitution reactions are possible in acetylene and 1-alkynes (terminal alkynes).

**(A) ACIDITY OF TERMINAL ALKYNES**

The acidic hydrogen of alkynes can be removed by a base



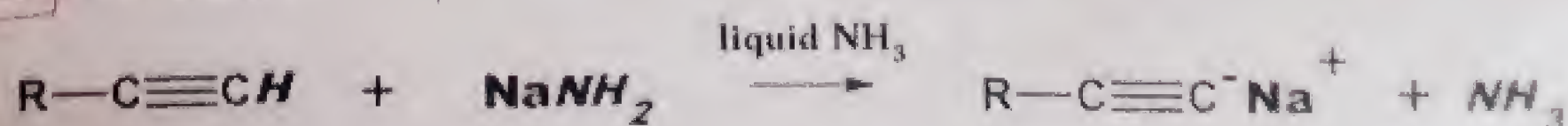
- In ethyne and other terminal alkynes like propyne, the hydrogen atom is bonded to the carbon atoms with sp-s overlap.
- An sp hybrid orbital has 50% s-character in it and makes the carbon atoms more electronegative. Thus, the sp-hybridized carbon atom of a terminal alkyne pulls the electrons more strongly making the attached hydrogen atom slightly acidic.



- This  $\text{H}^{\delta+}$  can be substituted with metal. Thus substitution reaction occurs due to  $\text{H}^{\delta+}$ .

**Examples:**

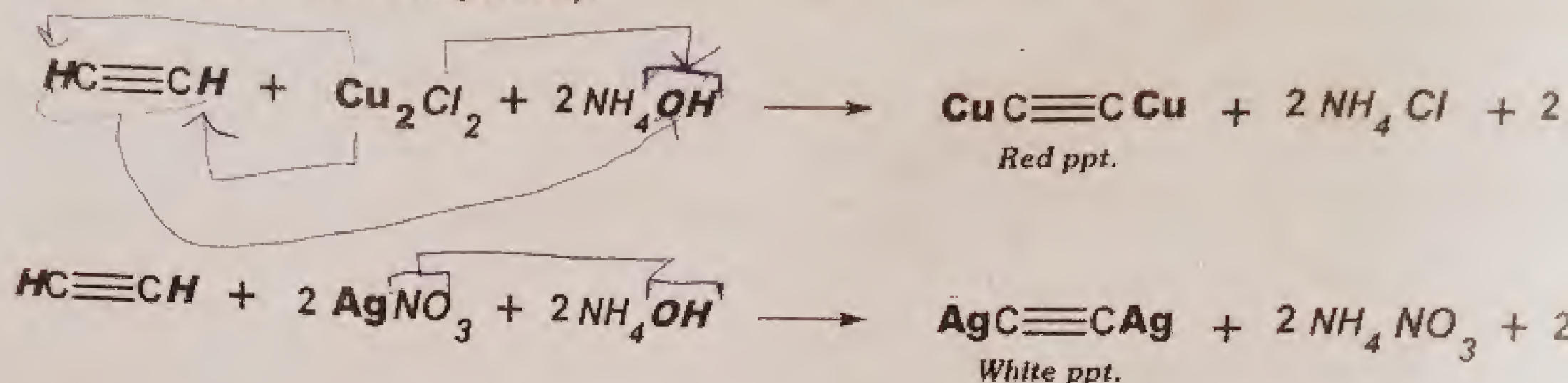
- When 1-alkyne or ethyne is treated with sodamide in liquid ammonia or passed over molten sodium, alkynides or acetylides are obtained.



Sodium acetylide is a very valuable reagent for chemical synthesis and is essentially rare in nature.

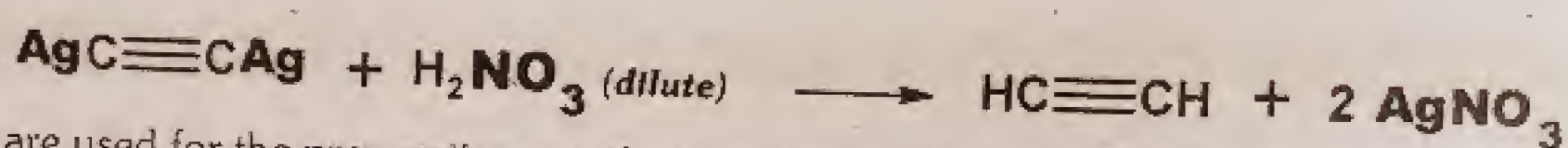
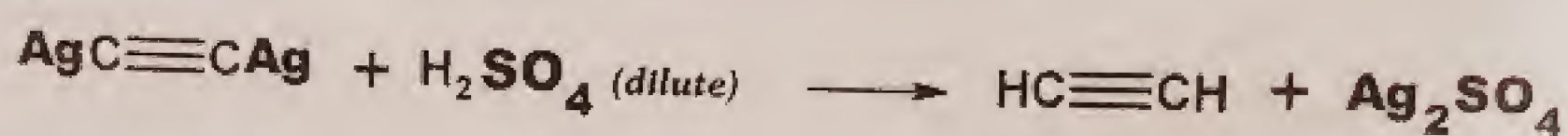


- (ii) Acetylides of copper and silver are obtained by passing acetylene in the ammoniacal solution of copper chloride and silver nitrate respectively.



Thus, these reaction can be used to detect 1-alkynes (terminal alkynes)

- Silver and copper acetylides react with acids to regenerate alkynes.



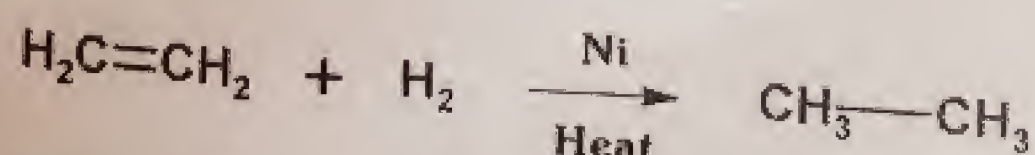
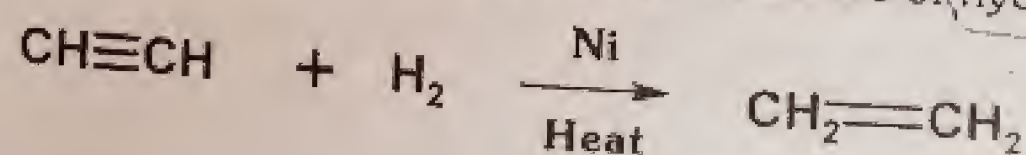
These alkynides are used for the preparation, purification separation, and identification of alkynes.

## (B) ADDITION REACTIONS OF ALKYNES

- Alkynes undergo addition reactions just like alkenes.
- The high electron density of the  $\pi$ -bonds makes them nucleophilic.
- Two factors influence the relative reactivity of alkynes compared to alkenes:
  - increased nucleophilicity of the starting p system, and
  - stability of any intermediates (for example carbocations)

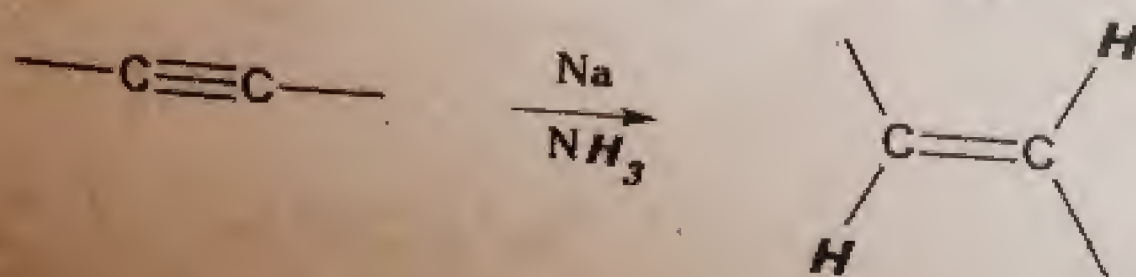
### (1) HYDROGENATION

- Alkynes react with hydrogen gas in the presence of suitable catalysts like finely divided Ni, Pt or Pd.
- In the first step alkenes are formed which then take up another molecule of hydrogen to form an alkane.



### (2) DISSOLVING METAL REDUCTION

Alkynes can be reduced to *trans*-alkenes using Na in  $\text{NH}_3$  (liq.)



**Remember!**

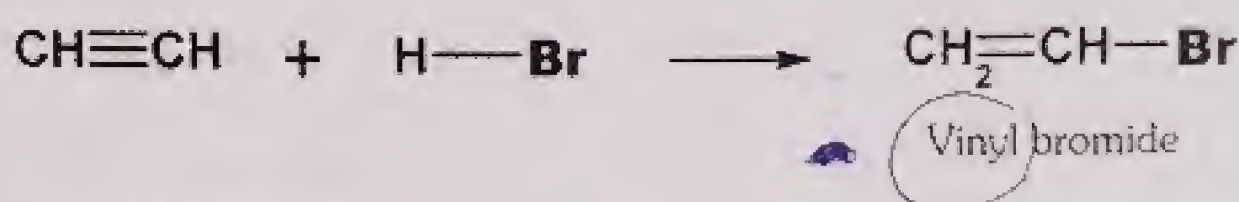
If two groups add on same side is called *syn*-addition  
If two groups add on opposite side, it is called *anti*-addition.



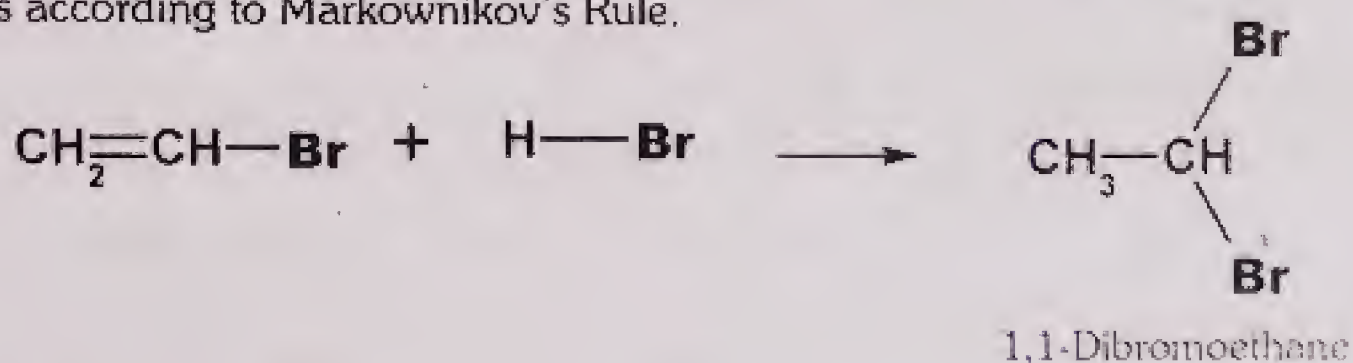
- This reaction is stereoselective because it gives only the *trans*-alkene via an anti-addition.
- The reaction proceeds via single electron transfer from the Na with H coming from the  $\text{NH}_3$ .
- The stereochemistry of this reaction is opposite to that of catalytic hydrogenation (*syn*-addition).
- These reaction conditions do not reduce alkenes, hence the product is the alkene.

### (3) HYDROHALOGENATION

Alkynes react with hydrogen chloride and hydrogen bromide to form dihaloalkenes. The reaction occurs in accordance with Markownikov's rule.

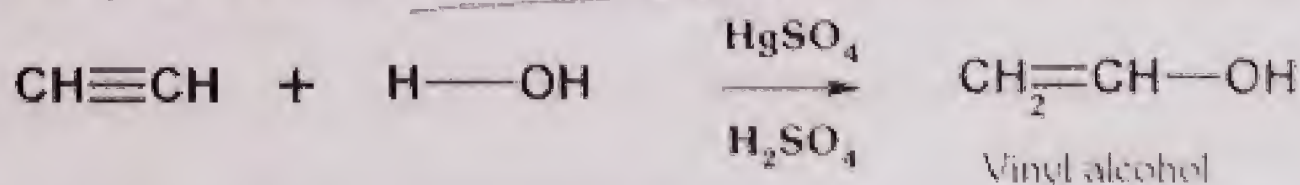


Second addition is according to Markownikov's Rule.



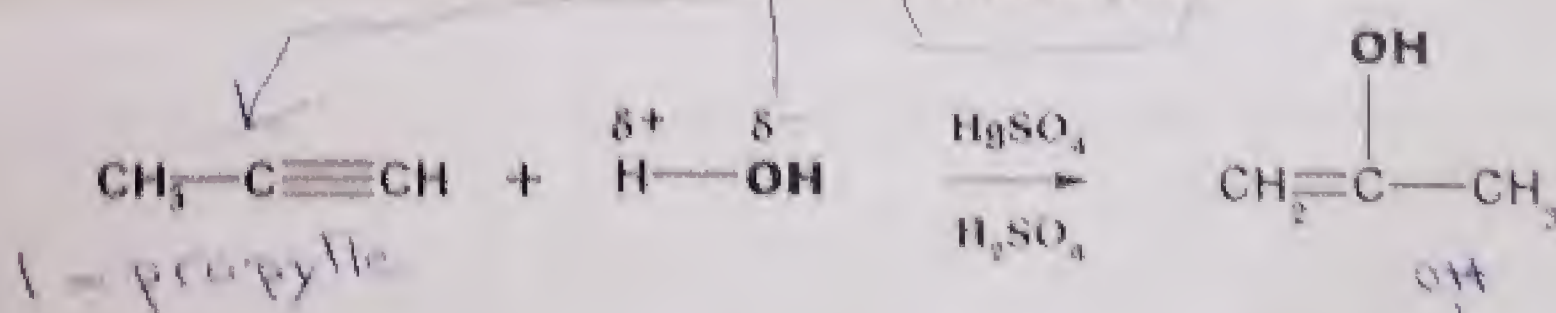
### (4) HYDRATION

Water adds to acetylene in the presence of mercuric sulphate dissolved in sulphuric acid at  $75^\circ\text{C}$ .



#### Rearrangement of Alcohol:

Vinyl alcohol is an unstable. It has the hydroxyl group attached to a doubly bonded carbon atom and isomerizes to acetaldehyde.

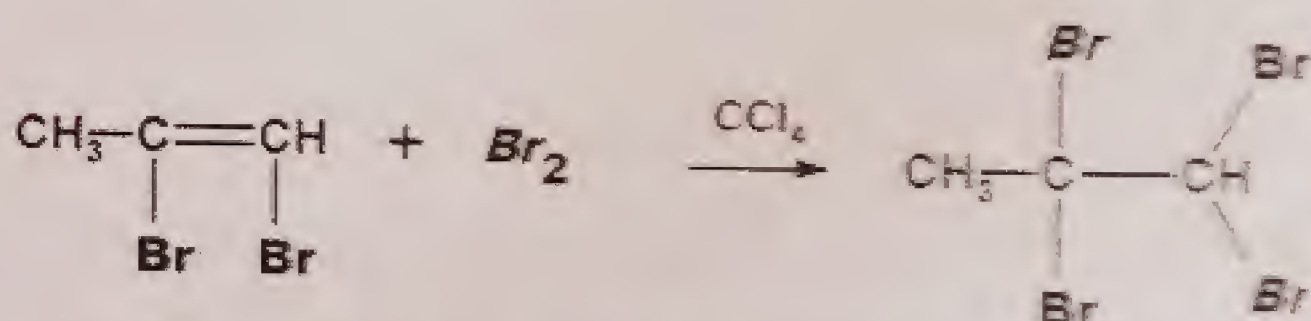
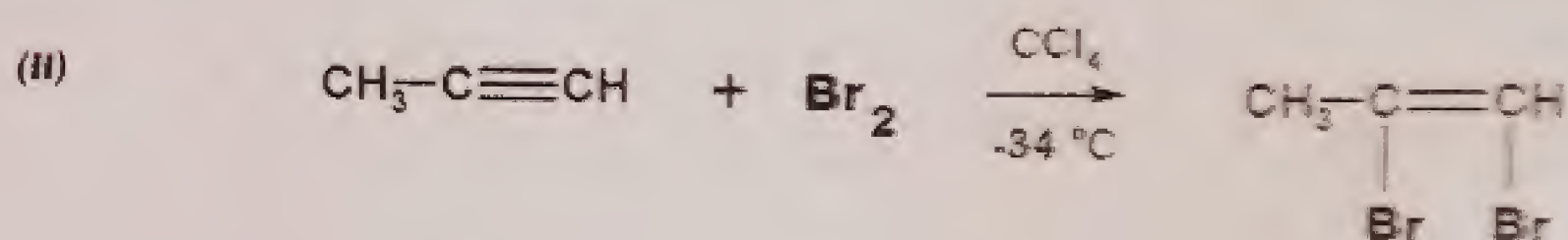
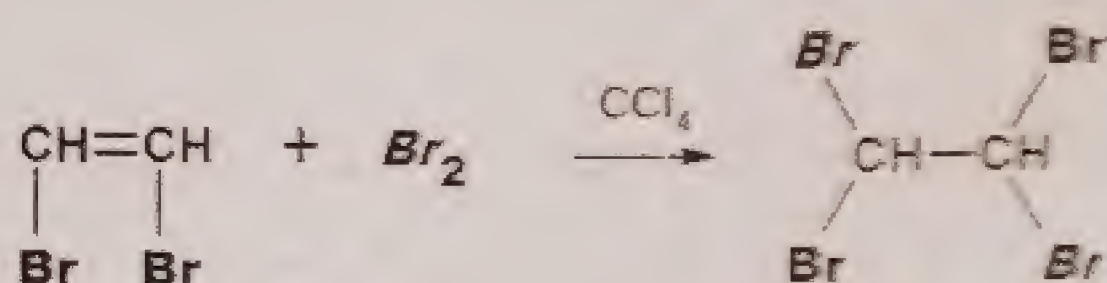
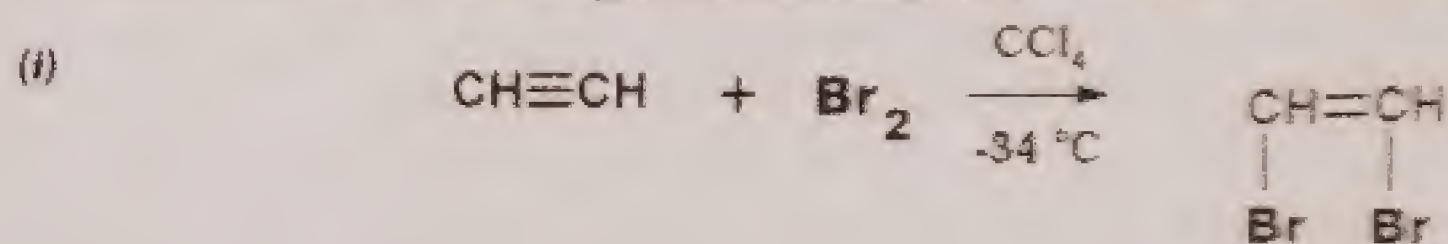


This reaction is industrially important because aldehydes can be prepared by this method.



### (5) BROMINATION

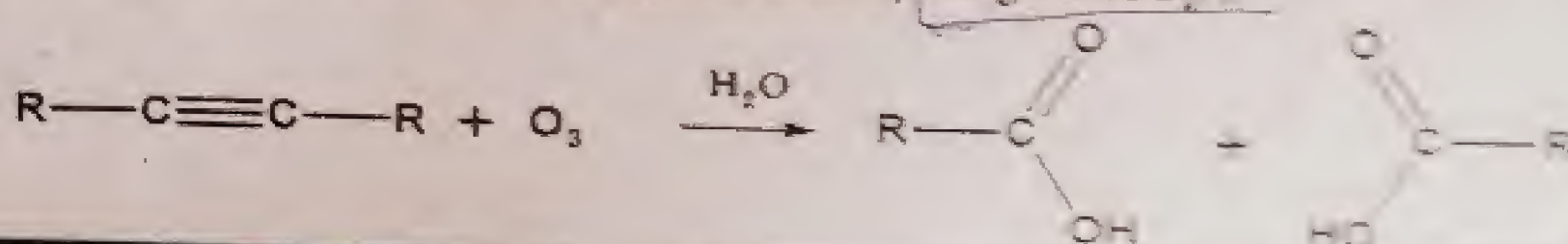
Chlorine and bromine add to the acetylenic triple bond in the presence of Lewis acid as catalyst:



The Halogenation may be stopped at the dihaloalkene stage because the double bond of dihaloalkene is less nucleophilic than even triple bond itself.

### (6) OZONOLYSIS

When ozone reacts with alkyne followed by aqueous work up we get  $2\text{RCOO}_2\text{H}$ .

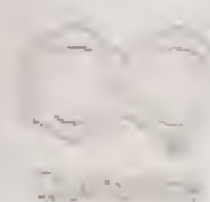
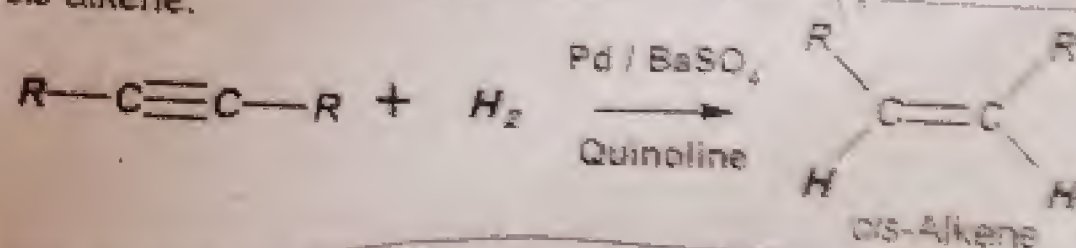


### QUICK QUIZ-5

What are reducing agent would you use to convert an alkyne to a

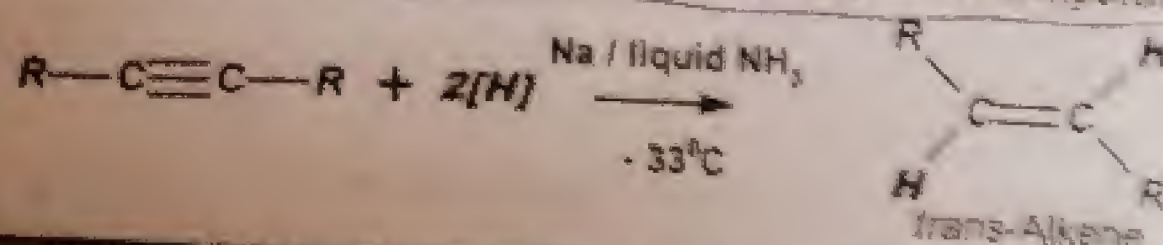
#### (i) cis-Alkene

The catalyst is finely divided Pd supported on  $\text{BaSO}_4$  and poisoned with quinoline. It is called Lindlar's catalyst. The product is cis-alkene.



#### (ii) trans-Alkene

It can also be done by treating alkynes with  $\text{Na/liq NH}_3$  at low temperature. The product is trans-alkene.



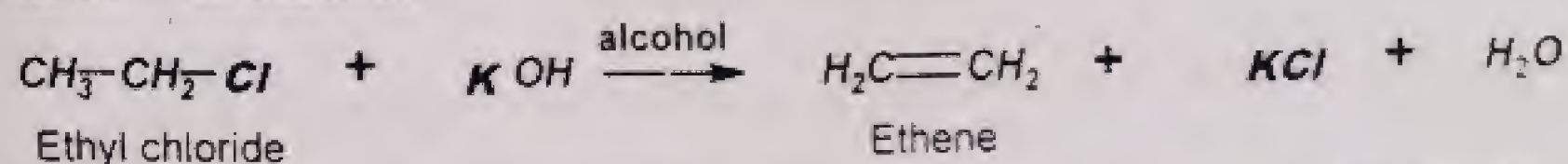


## SOME IMPORTANT CONVERSIONS

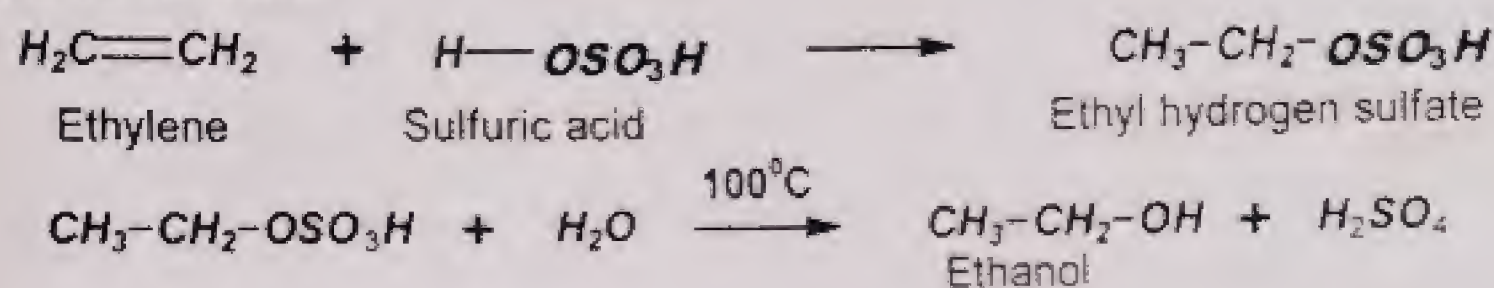
### (i) Methane to Ethane.



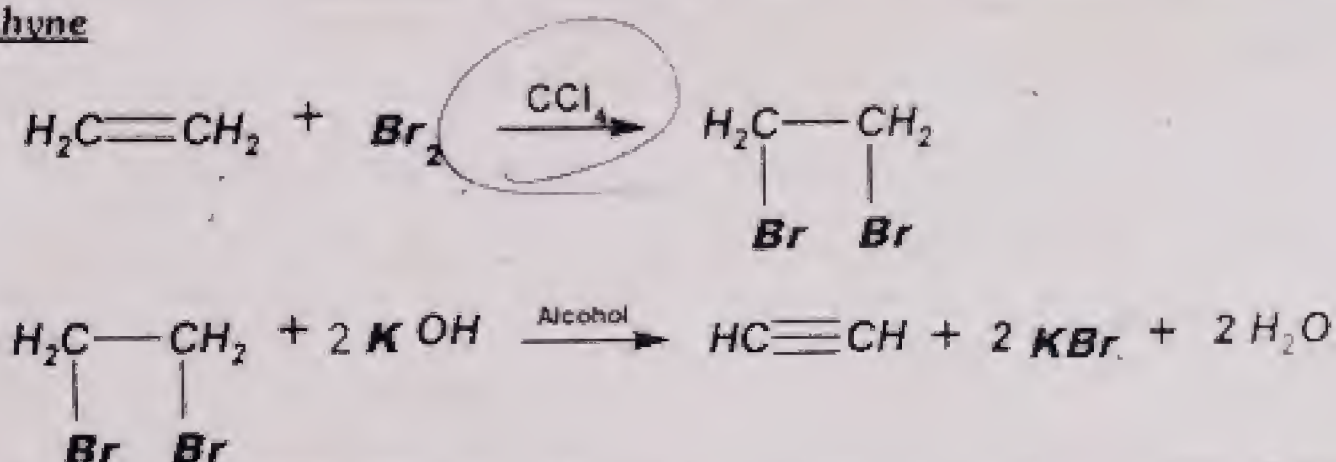
### (ii) Ethyl chloride to ethene.



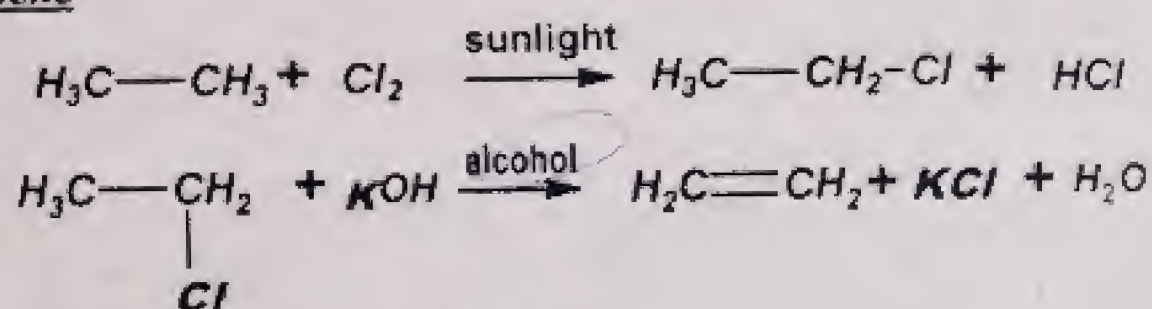
### (iii) Ethene to ethyl alcohol



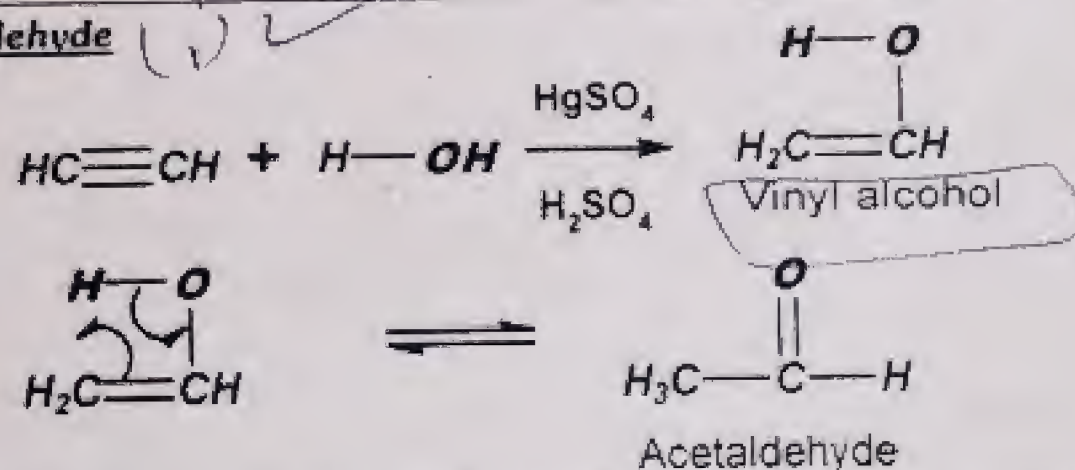
### (iv) Ethene to ethyne



### (v) Ethane to Ethene

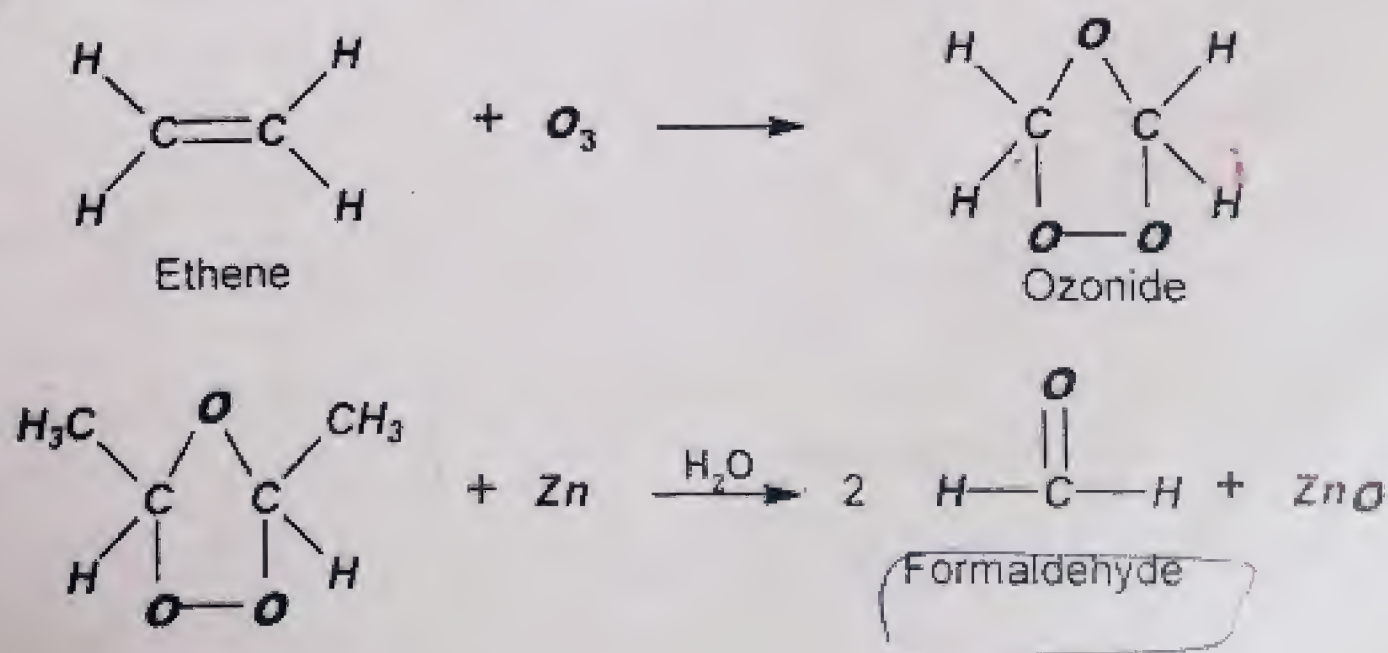


### (vi) Ethyne to Acetaldehyde



Similarly Propyne to Acetone

### (v) Ethene to formaldehyde





# BENZENE AND SUBSTITUTED BENZENES

## Important Information

Discovered by:	Michael Faraday
Isolated by:	Hoffmann from
Molecular Formula:	$C_6H_6$
Molecular weight:	$78 \text{ g mol}^{-1}$
Special Features:	(i) Resonance. (ii) Electrophilic Substitution Reactions

- Michael Faraday discovered benzene in 1825, during the destructive distillation of vegetable oil.
- Hoffmann isolated it from coal tar.
- As a functional group, benzene and substituted benzenes are called **arenes**.

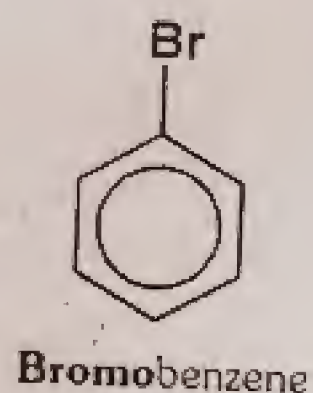
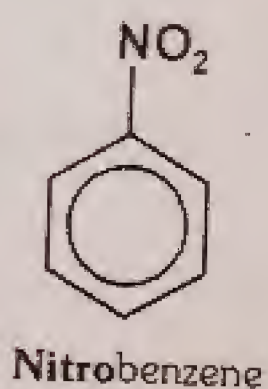
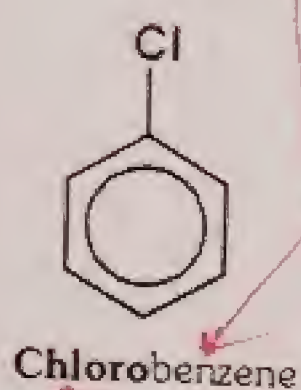
## NOMENCLATURE

### MONOSUBSTITUTED BENZENES

#### (a) Common System Naming:

The following procedures are adopted for naming *mono-substituted benzenes*:

- (1) Parent name is benzene and the substituent is indicated by a prefix, e.g.,

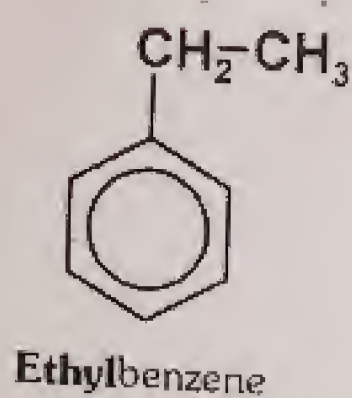
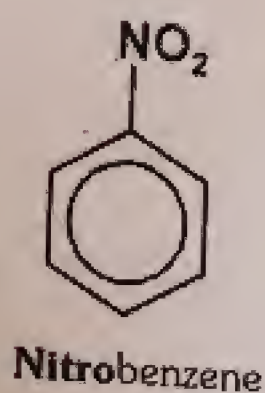
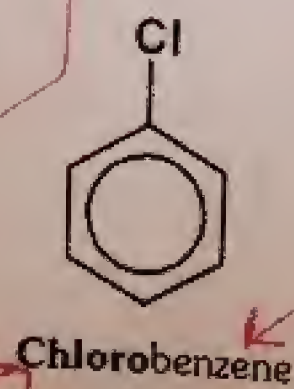


- (2) The substituent and the benzene ring taken together may form a new parent name. The largest parent name is preferred e.g.,  $C_6H_5CH_3$  may be named as: (i) Methyl benzene, (ii) Phenyl methane. According to "the largest rule" methyl benzene is preferred. (Since benzene is the larger parent than methane)

#### (b) IUPAC System of Naming:

- (1) Mono-substituted derivatives of benzene are named by prefixing the name of substituted to the word 'benzene'.

Example:



- (2) Many aromatic compounds have been known by their common or trivial names which are still in use. I.U.P.A.C. system retains these names: A few are given below:

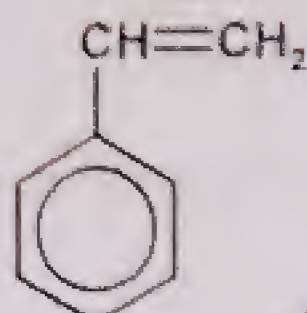




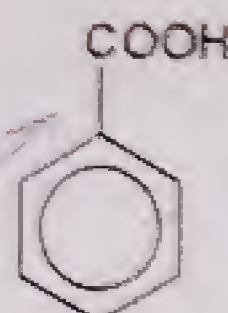
Toluene



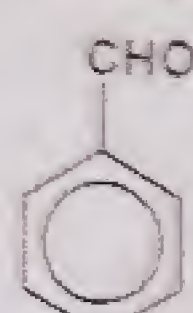
Aniline



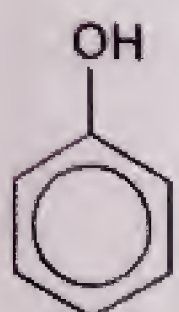
Styrene



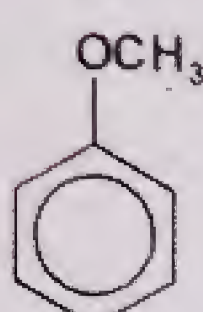
Benzoic acid



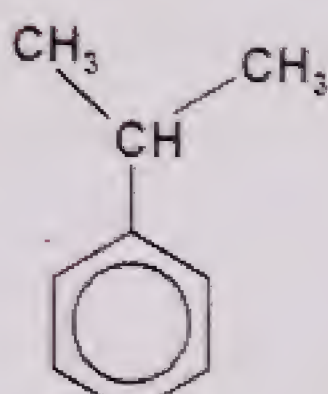
Benzaldehyde



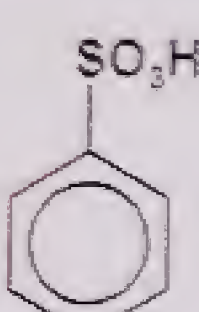
Phenol



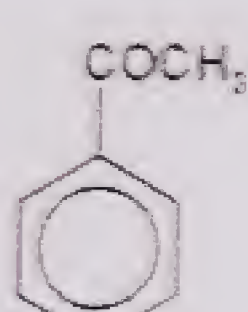
Anisole



Cumene



Benzenesulfonic acid

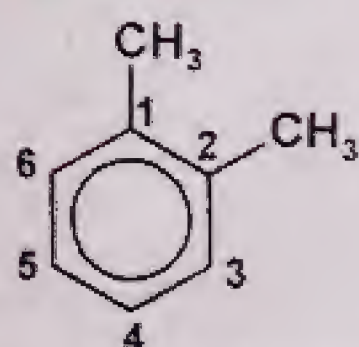


Acetophenone

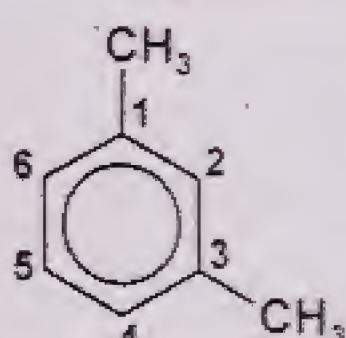
## DISTRIBUTED BENZENE

(1) When there are two substituents on benzene ring their relative positions are indicated

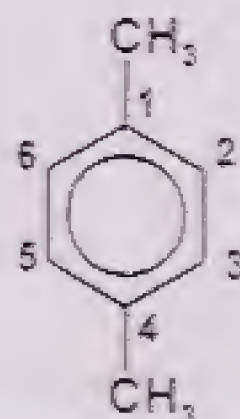
- by prefixes ortho (o), meta (m) and para (p) in common system of naming and
- by numerals while naming according to IUPAC system.



o-Dimethylbenzene  
(1,2-Dimethylbenzene)  
(o-Xylene)



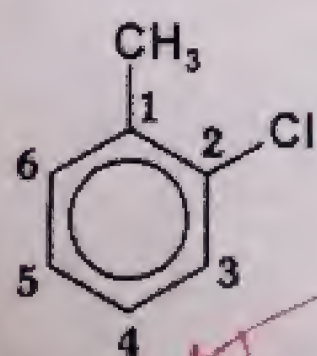
m-Dimethylbenzene  
(1,3-Dimethylbenzene)  
(m-Xylene)



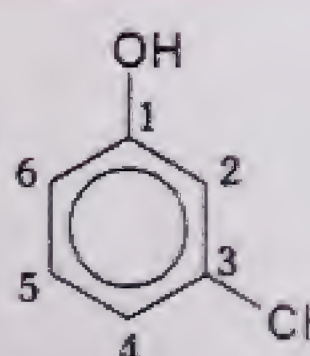
p-Dimethylbenzene  
(1,4-Dimethylbenzene)  
(p-Xylene)

(2) If the substituents are different and one of them is an alkyl group the numbering is started from the ring carbon which is linked to the alkyl group and the second substituent gets the lowest possible number.

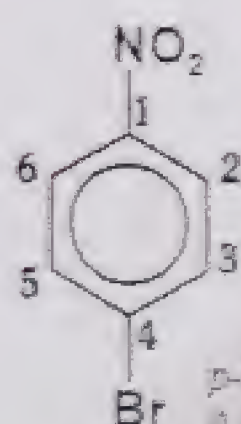
(3) When a common name is used, the substituent which is responsible for name, e.g.,  $\text{CH}_3$  in toluene, and  $\text{-OH}$  in phenol, is considered to be on carbon-1. Thus, numbering is started from the carbon of ring bearing that group and such a compound is named as derivative of that parent.



o-Chlorotoluene or  
2-Chlorotoluene (IUPAC)



m-Chlorophenol or  
3-Chlorophenol (IUPAC)

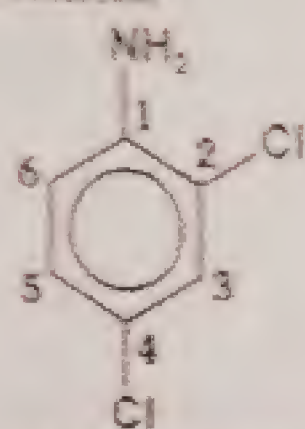


p-Bromonitrobenzene or  
4-Bromonitrobenzene (IUPAC)

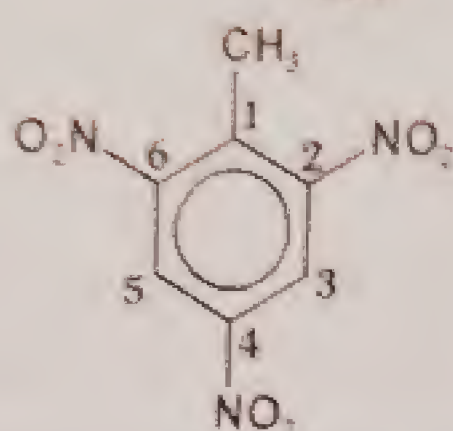
(4) When two substituents are different, they are usually put in alphabetical order.

(5) Poly-substituted benzenes are named by numbering the substituent to ring so as to give the substituents lowest possible numbers. The last named substituent is assumed to be at position number 1. This number is not indicated in the name.

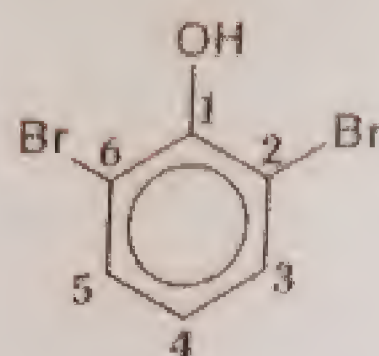




2,4-Dichloroaniline

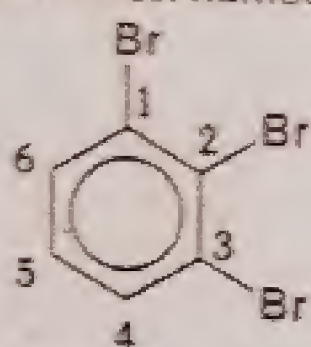


2,4,6-Trinitrotoluene (TNT)

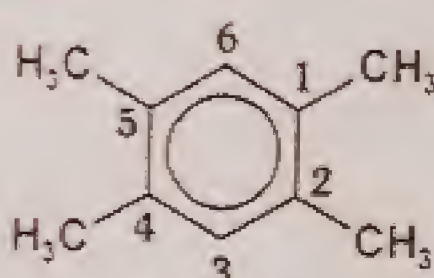


2,6-Dibromophenol

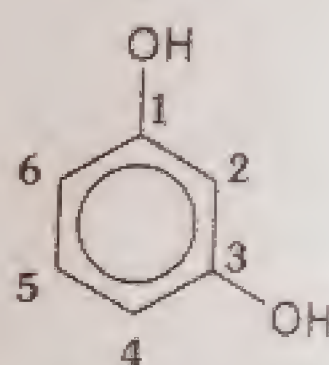
(6) If the substituents are all alike their positions are indicated by numbering the substituents in a manner so as to give the lowest number to the substituents.



1,2,3-Tribromobenzene

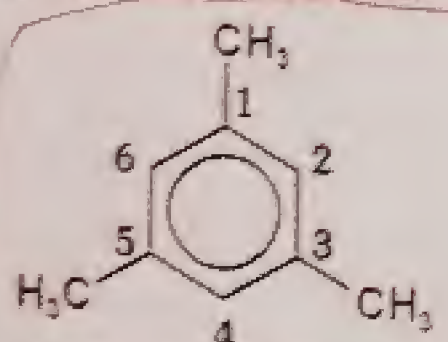


Durene or  
1,2,4,5-Tetramethylbenzene (IUPAC)

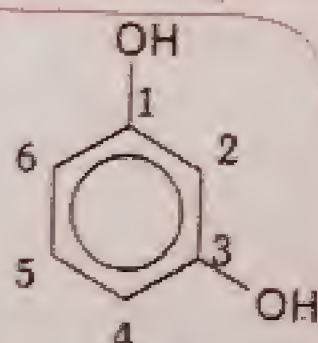


Resorcinol

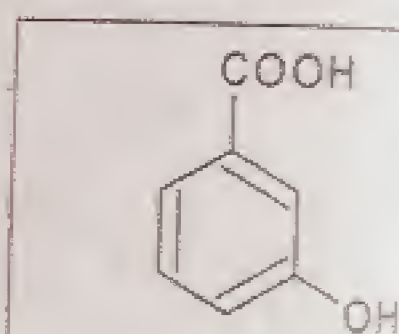
(7) Some poly-substituted benzenes are still known by their common name.



1,3,5-Trimethylbenzene  
(Mesitylene)



Resorcinol



3-hydroxybenzoic acid

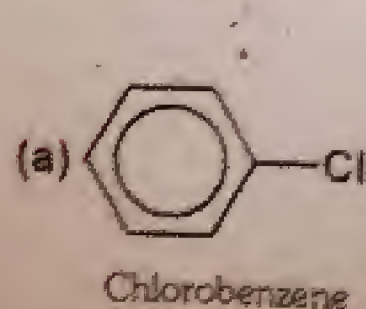
**Remember!**

If two different functional groups are present on benzene ring then it is better to check as per following priority list:  $-\text{COOH}$ ,  $-\text{CN}$ ,  $-\text{CHO}$ ,  $-\text{COCH}_3$ ,  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{OR}$ ,  $-\text{R}$ . The group which is earlier in the list has high priority. If  $-\text{COOH}$  and  $-\text{OH}$  are present, then  $-\text{COOH}$  will take high priority and thus compound will be called as benzoic acid.

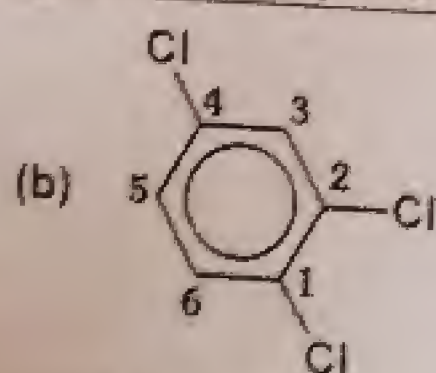
**Example**

**ACTIVITY:-**

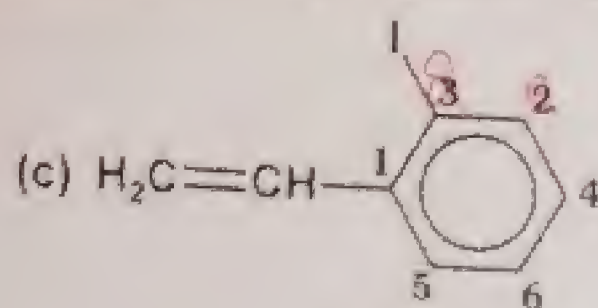
1- Give the suitable name to each of following:-



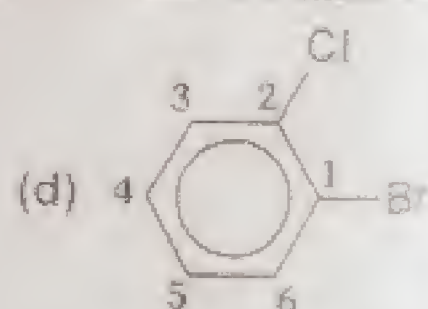
Chlorobenzene



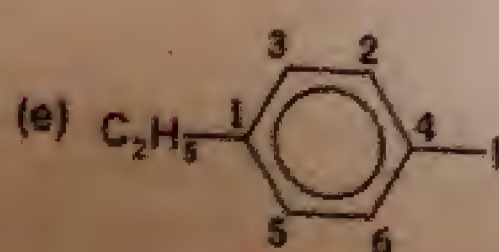
1,2,4-Trichlorobenzene



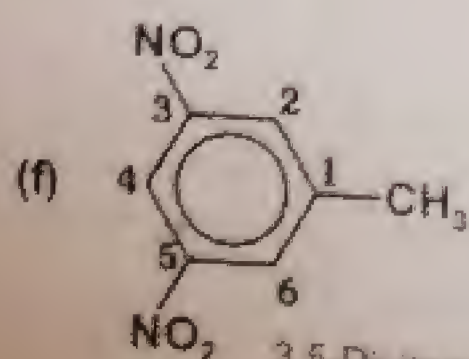
2-Iodostyrene



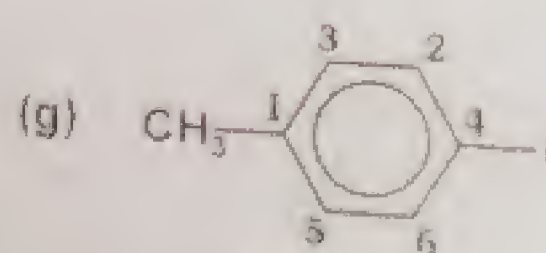
1-Bromo-2-chlorobenzene



1-Ethyl-4-iodobenzene



3,5-Dinitrotoluene

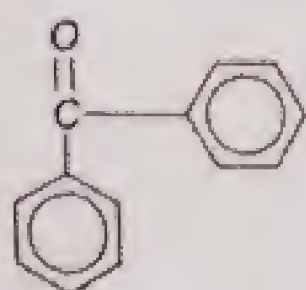


4-Iodotoluene

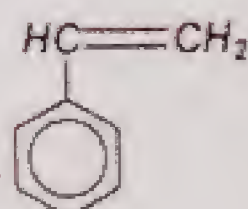


**MORE PRACTICE**

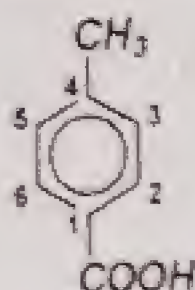
**AROMATICS**



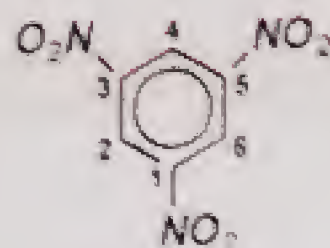
Benzophenone



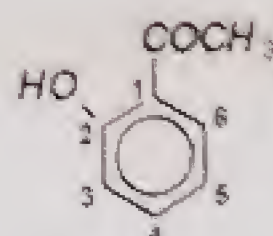
Vinylbenzene



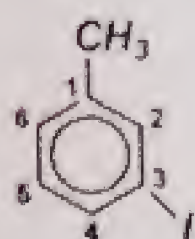
4-Methylbenzoic acid



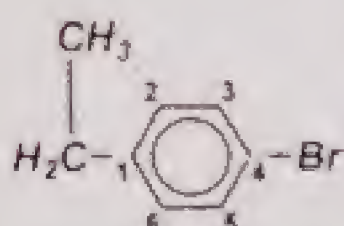
1,3,5-Trinitrobenzene



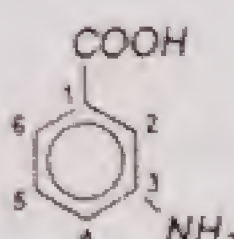
2-Hydroxyacetophenone



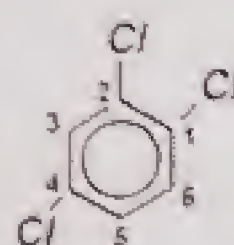
3-Iodotoluene



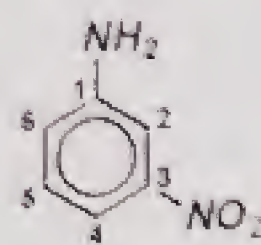
4-Bromoethylbenzene



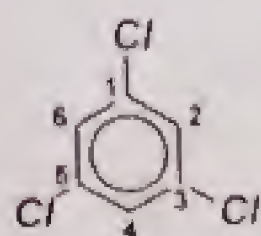
3-Aminobenzoic acid



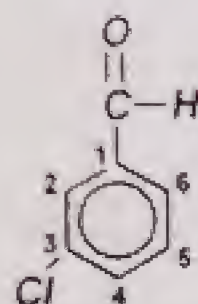
1,2,4-Trichlorobenzene



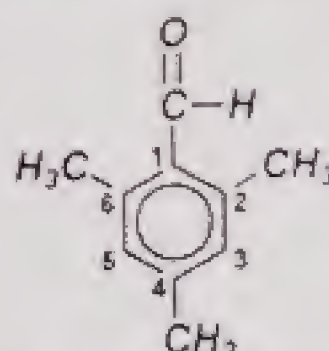
3-Nitroaniline



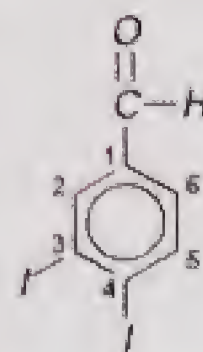
1,3,5-Trichlorobenzene



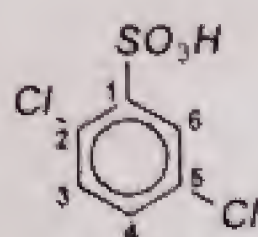
3-Chlorobenzaldehyde



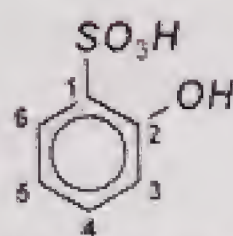
2,4,6-Trimethylbenzaldehyde



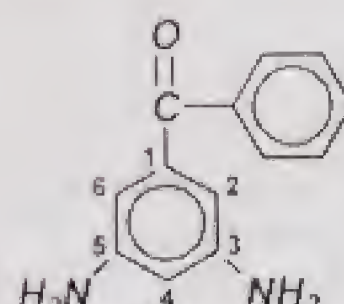
3,4-Diodobenzaldehyde



2,5-Dichlorobenzenesulfonic acid



2-Hydroxybenzenesulfonic acid



3,5-Diaminobenzophenone

**CYCLIC**



cyclopropane



cyclobutane



cyclopentane



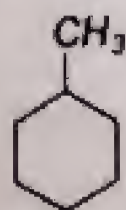
cyclohexane



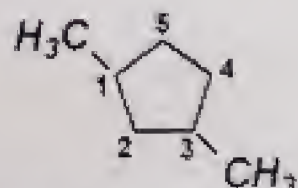
cycloheptane



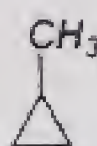
cyclooctane



Methylcyclohexane



1,3-Dimethylcyclopentane



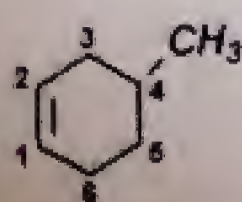
Methylcyclopropane



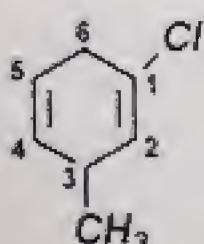
cyclohexene



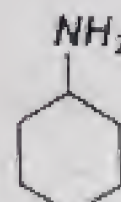
Cyclo-1,3-pentadiene



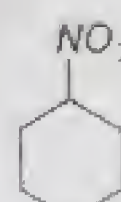
4-Methylcyclohexene



1-Chloro-3-methylcyclohexa-1,4-diene



Cyclohexanamine



Nitrocyclohexane



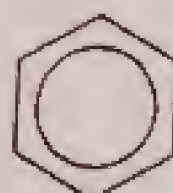
## PHYSICAL PROPERTIES:

In the absence of polar substituents, arenes are typical hydrocarbons. They are non-polar, have low melting and boiling points and low solubility in polar solvents.

## STRUCTURE (MOLECULAR ORBITAL ASPECTS)



Kekule structures



Robinson structure

- All twelve atoms in benzene,  $C_6H_6$ , lie in the same plane.
- Benzene has a planar, cyclic, conjugated structure.
- It contains alternating  $C=C$  and  $C-C$  bonds. Thus, two different Kekule structures are obtained. These are two equally valid resonance contributors.
- Alternatively, these two forms can be combined in the resonance hybrid and the conjugated system represented by a circle as in the Robinson structure.
- All the  $CC$  bonds are  $1.4 \text{ \AA}$  [between typical  $C=C$  ( $1.33 \text{ \AA}$ ) and  $C-C$  ( $1.54 \text{ \AA}$ ) distances].

### Which representation is best?

- In benzene all the  $CC$  bonds are known to be of equal length, so there are no  $C=C$  and  $C-C$ . This is best represented by the resonance hybrid in the Robinson form.
- However, the key to organic chemistry is to understand mechanisms and draw curved arrows to show the positions of the electrons. The Kekule structures give a more precise description of the electron positions.
- Hence, it is a good idea to use a Kekule representation.

### Limitations of Kekule's Structure

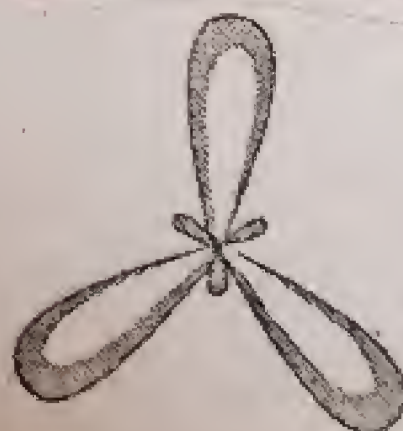
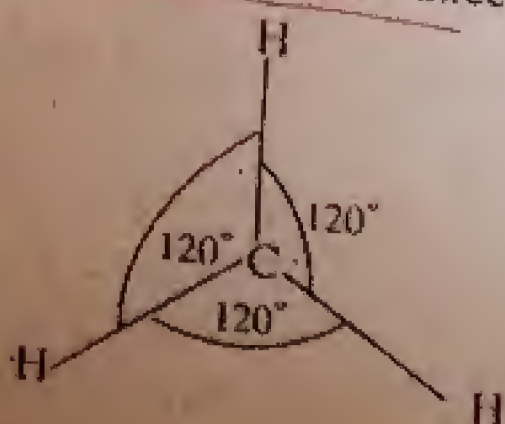
Kekule's structure failed to explain as to why

- (1) Benzene is less reactive
- (2) It shows dual character, i.e., it shows addition as well as substitute reaction.
- (3) It has less heat of formation, and
- (4) It has equal  $C-C$  bonds.

Exercise Q3 (4) (b). Explain the structure of benzene according to atomic orbital structure (or Molecular Orbital Structure).

## MOLECULAR ORBITAL TREATMENT OF BENZENE (or ATOMIC ORBITAL TREATMENT)

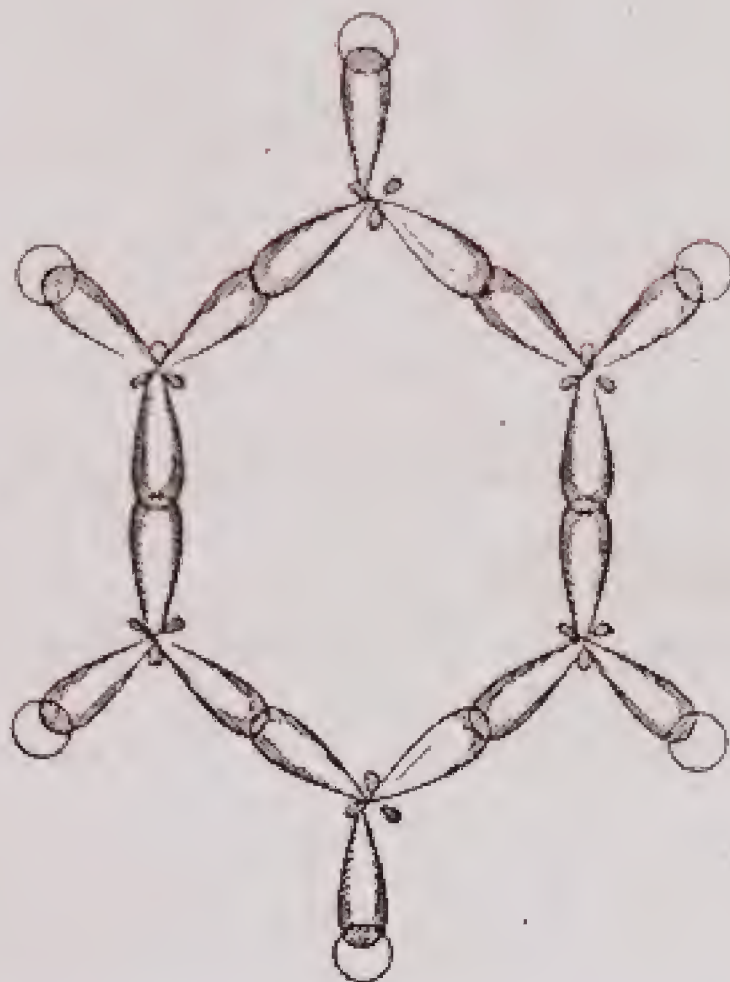
- Spectroscopic studies and X-rays analysis have shown that benzene is a regular, flat planar hexagon.
- All six hydrogen atoms are co-planar with six carbon atoms.
- The bond angles are:
  - (i)  $C-\hat{C}-C = 120^\circ$ , and
  - (ii)  $C-\hat{C}-H = 120^\circ$
- Thus each  $C$ -atom is in a state of  $sp^2$ -hybridization because each  $C$ -atom is attached to three atoms.
- Each  $sp^2$ -hybridized carbon atom has three  $sp^2$ -orbitals and one unhybridized  $2p_z$  orbitals.





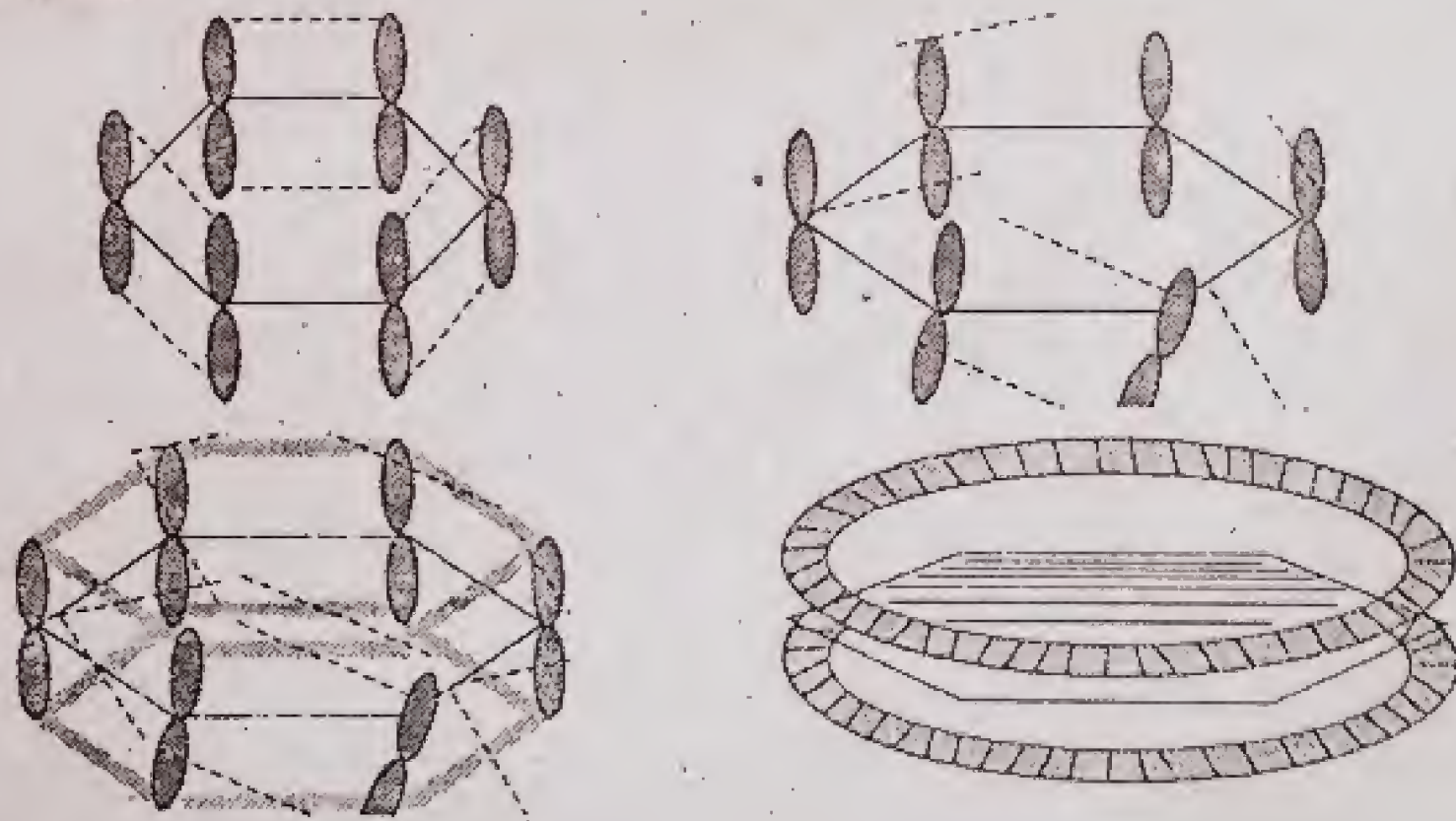
**Sigma Framework of benzene:**

The combination of six  $sp^2$ -hybridized carbon atoms and overlap of six hydrogen atoms ( $1s^2$ ) produces the following sigma frame work of benzene.



**Delocalized pi-bonding:**

- Six atomic p-orbitals one on each C-atom, are present perpendicular to this sigma bonding.
- Each p-orbital overlaps in parallel manners with neighbouring p-orbitals to give a continuous sheath of negative charges as:



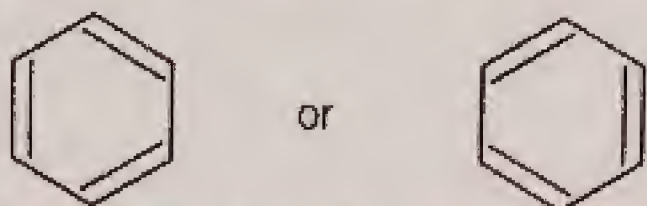
**Conclusions:**

- The parallel overlap all six p-orbitals form an extensive delocalized pi-bonding which spreads over all the carbon nuclei of benzene.
- Delocalization of p-orbitals over the entire ring produces sandwich like structure of benzene and it decreases the energy of molecule. Thus, the molecule becomes more stable and less reactive.
- According to this molecular orbital picture each carbon-carbon bond in benzene consists of one full sigma-bond and half a pi-bond. Thus, the carbon-carbon bond lengths are equal and benzene shows substitution as well as addition reactions.



## QUICK QUIZ-6

Criticize the following statement: "Benzene is a mixture of molecules most of which have the structure."



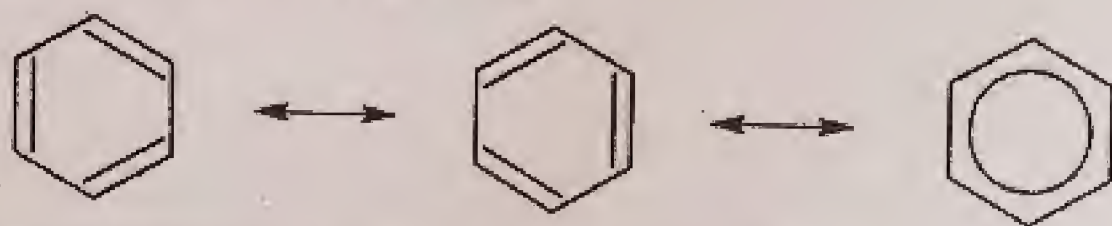
These two structures explain most of the experimental properties of benzene. So, it can be said that if benzene is a mixture of molecules than most of these have the above structures.

However, these structures show that benzene contains double bonds, therefore, it should give reactions of unsaturated hydrocarbons i.e. addition reactions. However, benzene mostly gives substitution reactions like saturated hydrocarbons. Hence, these two are not actual structures of benzene. These can be considered as hypothetical structures.

### MODERN REPRESENTATION OF BENZENE

With the help of molecular orbital behaviour we conclude that benzene has

- A regular hexagonal structure with an inscribed circle.
- A hexagon has alternate double and single bonds.



### RESONANCE, RESONANCE ENERGY AND STABILIZATION

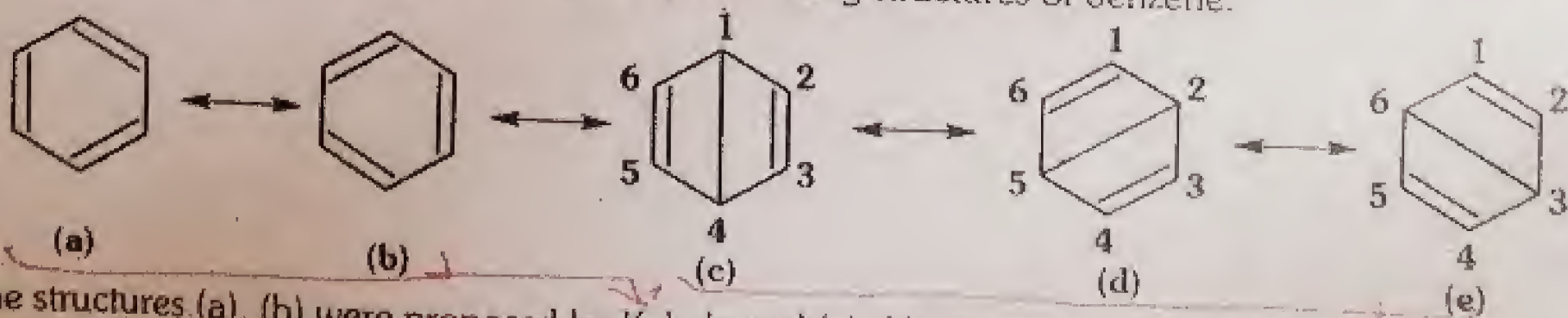
#### (I) RESONANCE

The possibility of different pairing schemes of valence electrons of atom is called resonance" and the different structures thus arranged are called "Resonance Structures".

**Explanation:**

The resonance is represented by a double-headed arrow.

**Example:** The following different pairing schemes of the fourth valence (the p-electrons) of carbon atoms are possible in benzene. This gives the following resonating structures of benzene:



- The structures (a), (b) were proposed by Kekule and (c), (d), (e) were proposed by Dewar.
- The stability of a molecule increases with increase in the number of its resonance structures. Thus molecule of benzene is chemically quite stable.
- The actual structure of benzene is a resonance hybrid of all five structures.
- The Kekule's structure have the larger contribution and Dewar's structures have the lesser contribution. Therefore, benzene molecule can be represented by either of the two Kekule's structure.





- The three alternate single and double bonds in the above structure are called conjugate bonds or resonating bonds.
- Since the structure of benzene is a resonance hybrid, therefore all the C-C bond lengths are equal. However, these bonds are different from those in alkanes, alkenes and alkynes. It is intermediate between those in alkanes and alkenes.
- The resonating single and double bonds in benzene can better be represented as follows.

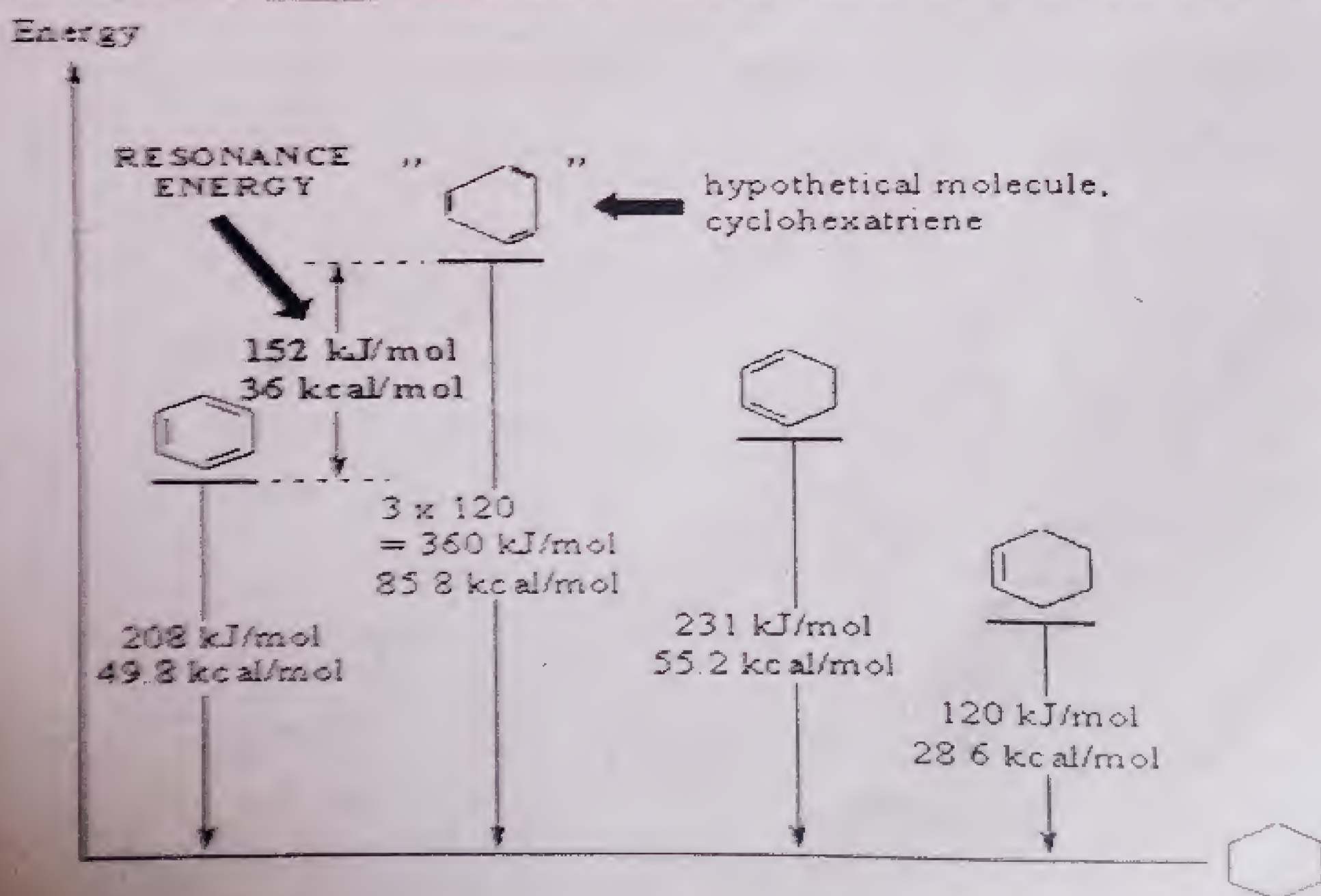


### 10. RESONANCE ENERGY

The resonance energy of a compound is a measure of the extra stability of the conjugated system compared to the corresponding number of isolated double bonds. It can be calculated from experimental measurements.

**Explanation**

- The diagram shows the experimental heats of hydrogenation,  $\Delta H_h$ , for three molecules, benzene, 1,3-cyclohexadiene and cyclohexene.
- Under appropriate conditions they can all be reduced to the same product, cyclohexane.
- The  $\Delta H_h$  for cyclohexene is 120 kJ/mol.
- In hypothetical "cyclohexatriene" molecule, the double bonds are assumed to be isolated from each other. Thus, its  $\Delta H_h$  should be three times of  $\Delta H_h$  for cyclohexene ( $120 \times 3 = 360$  kJ/mol). Thus, during hydrogenation of "cyclohexatriene" 360 kJ/mol energy should be released from three isolated C=C bonds.
- However, the experimental  $\Delta H_h$  for benzene is 208 kJ/mol.
- So, the difference between experimental value for benzene and that of hypothetical "cyclohexatriene" is 152 kJ ( $360 - 208 = 152$ ) or 36 kcal/mol.
- Thus, benzene is 152 kJ/mol more stable than the hypothetical system. This is the resonance energy for benzene.





The more red an area, the higher the electron density and the more blue an area is, the lower the electron density. College Chemistry: Federal Board: Part II

CH # 16: Hydrocarbons

## REACTIVITY AND REACTIONS

The image shows the electrostatic potential for benzene.

- The more dark area is the region of higher electron density and the less dark area is the region of lower electron density.
- Hence, the aromatic  $\pi$ -system is nucleophilic in character.
- For arenes, there are two types of reactions:
  - ✓ Reactions of electrophiles directly on the aromatic ring, and
  - ✓ Reactions of the substituents (since the neighboring aromatic group influences its reactivity).
- For reactions directly on the aromatic ring:
  - ✓ The cyclic array of  $\pi$ -bonds is a region of high electron density so arenes are typically nucleophiles (unlike alkenes and alkynes).
  - ✓ Alkenes and alkynes undergo addition reactions. However, arenes typically undergo substitution reactions in which a group (usually  $-H$ ) is replaced and the aromatic system is retained.
  - ✓ The stability of the aromatic system favours substitution over addition. It is because addition would destroy the aromatic system.

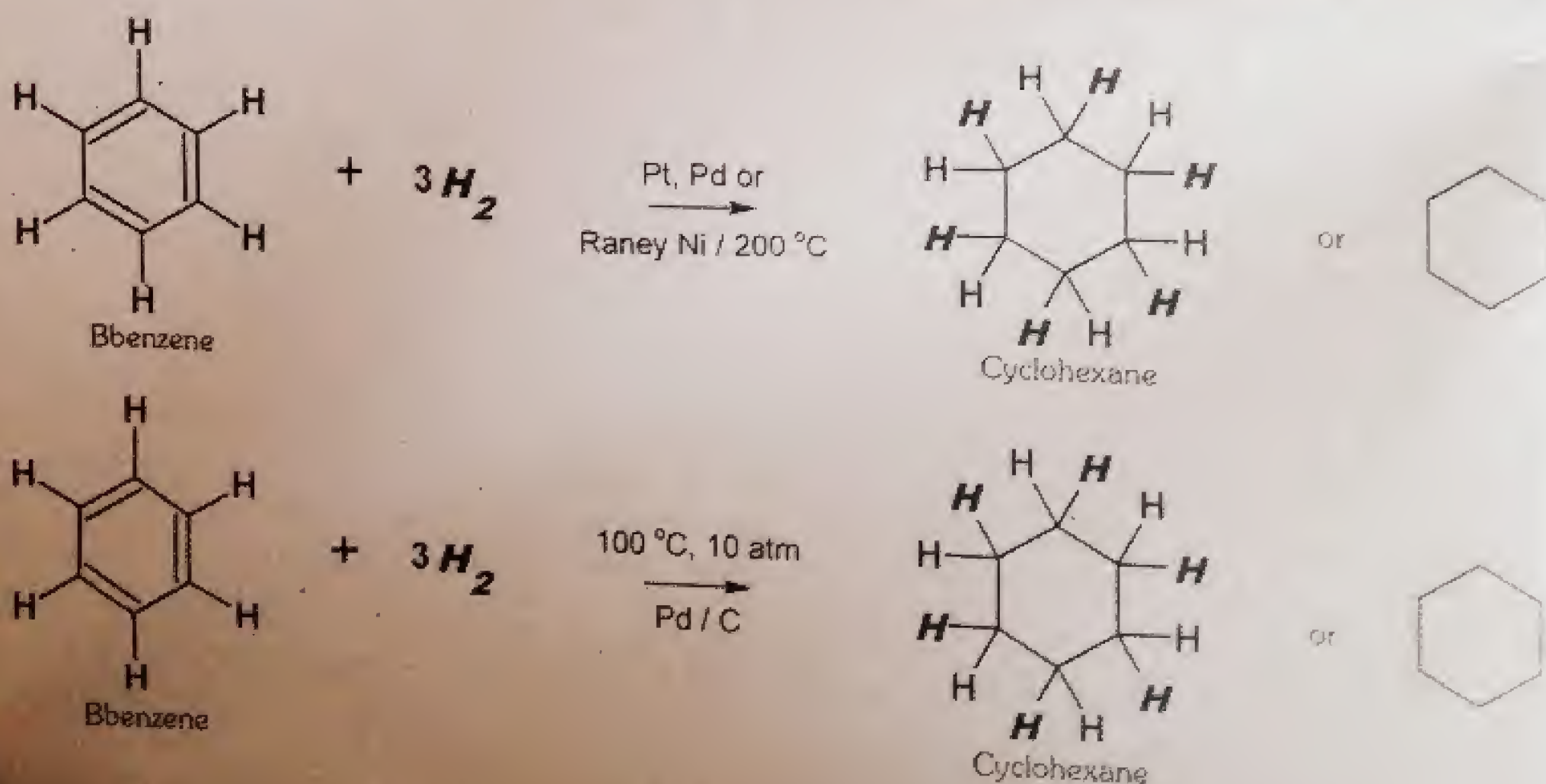


### (A) ADDITION REACTIONS

- Benzene is highly unsaturated compound. It has three double bonds in it. But it does not undergo addition reaction happily. The reason is that it shows resonance. The delocalization of  $\pi$ -electrons makes it extra stable.
- So for addition reaction benzene requires more vigorous condition than that of alkenes and alkynes.

#### (1) CATALYTIC HYDROGENATION

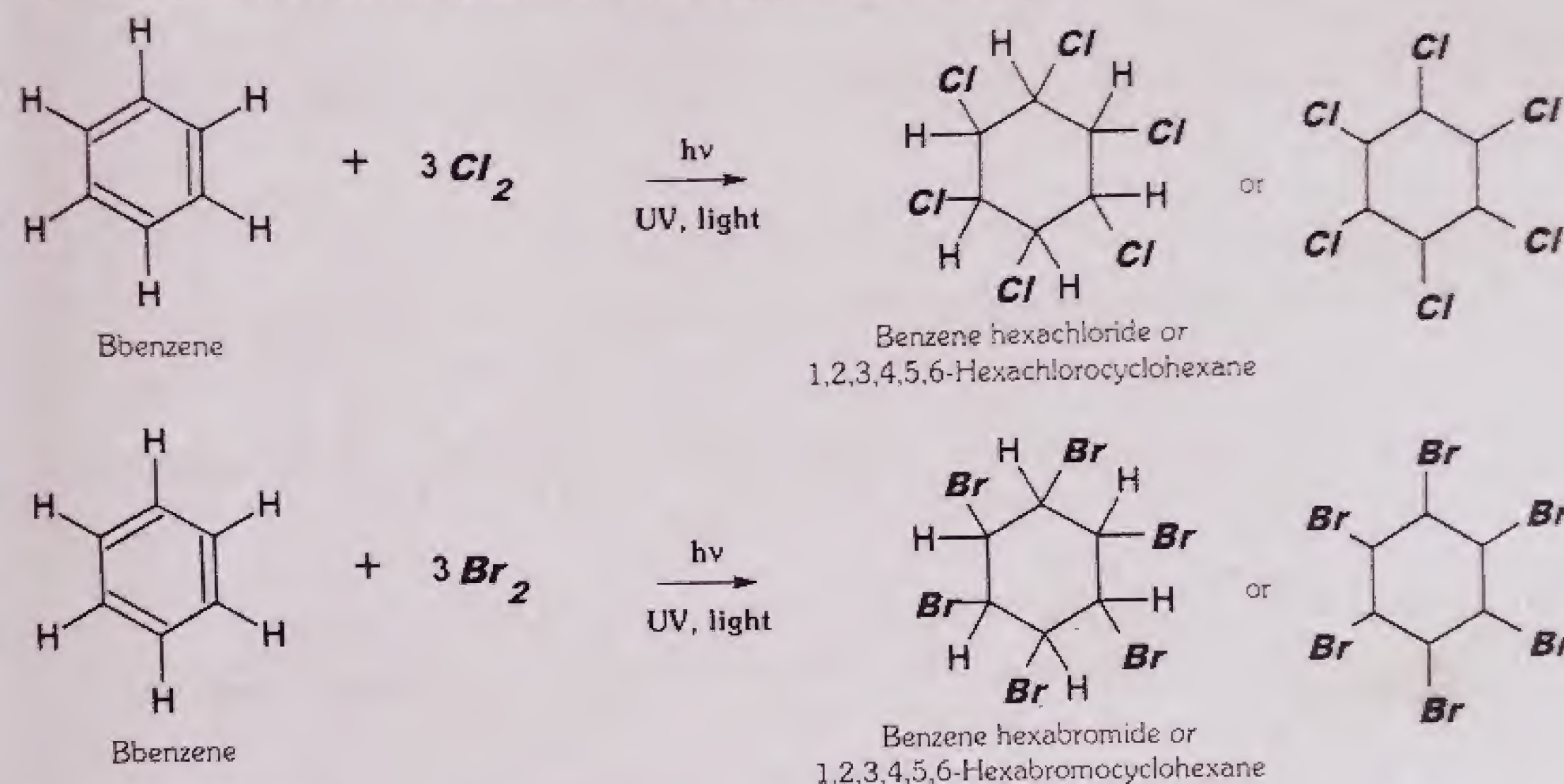
- Benzene can be hydrogenated in the presence of a catalyst as Pt, Pd, or Raney Ni only at higher temperature and pressures.
- If we use the metals like Ru, Rh, supported at carbon then hydrogenation becomes easier.





## 2) ADDITION OF HALOGENS

- Benzene can add three molecules of chlorine or bromine under the influence of light.
- The benzene ring becomes saturated, and we get benzene hexachloride and benzene hexabromide.
- This reaction shows that benzene has three double bonds in the ring.



### Reaction of F<sub>2</sub> and I<sub>2</sub>:

The reaction of F<sub>2</sub> with benzene is very vigorous, while with I<sub>2</sub> it is very slow.

### Conclusion:

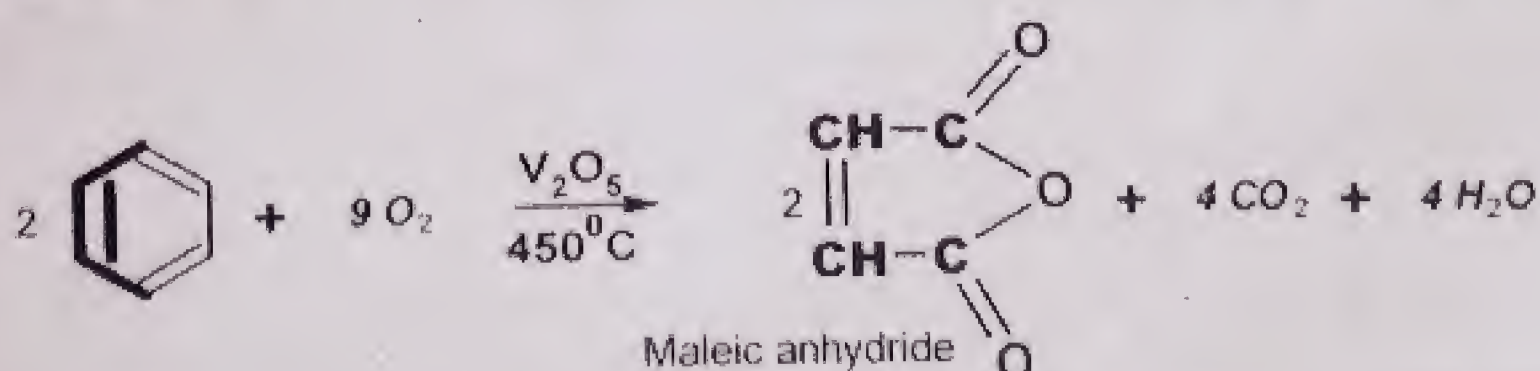
The addition reaction of hydrogen and chlorine show that benzene is unsaturated hydrocarbon and has three double bonds in it.

## (B) OXIDATION REACTIONS

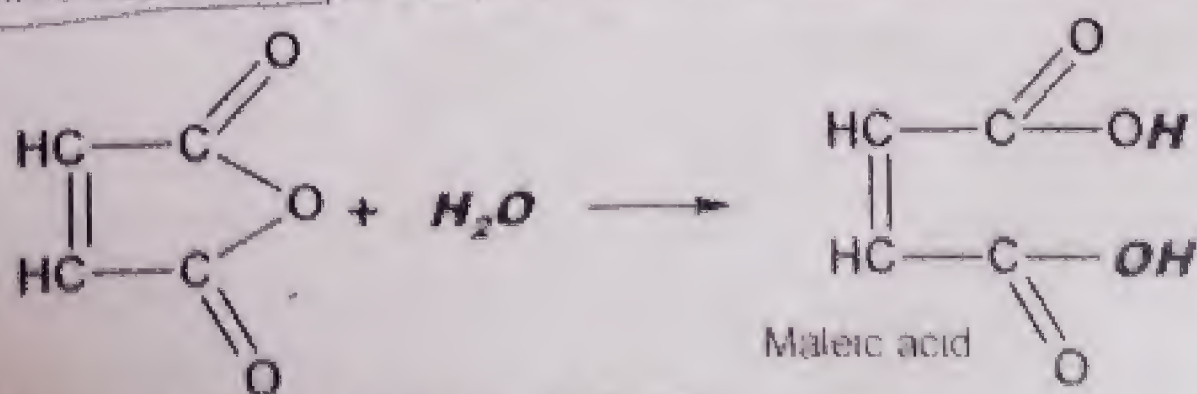
- Benzene is stable towards general oxidizing agents. However, it can be oxidized under certain conditions

### (1) CATALYTIC OXIDATION

When benzene is oxidized with air in the presence of V<sub>2</sub>O<sub>5</sub> at 450°C, then we get maleic anhydride



- This is commercial method for the preparation of maleic anhydride which on hydrolysis give maleic acid.



- Benzene is not oxidized by KMnO<sub>4</sub> or K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>



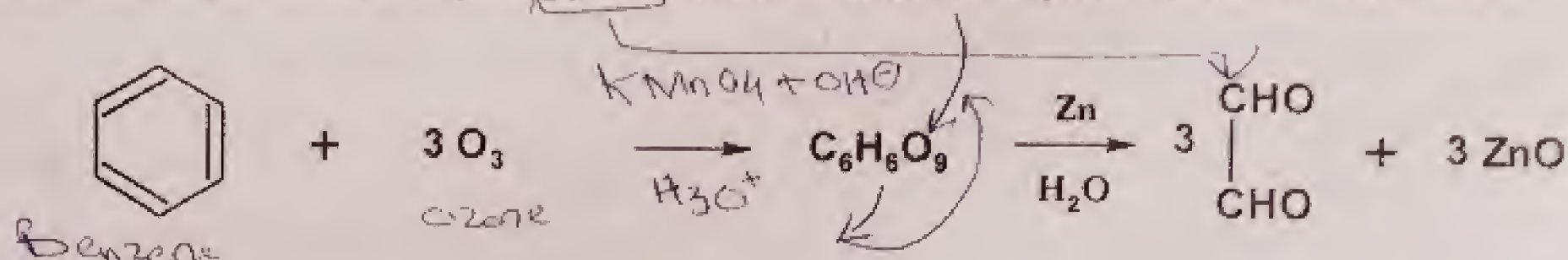
## (2) COMBUSTION

When benzene is burnt in the presence of air or oxygen,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are produced, just like other aliphatic hydrocarbons.



## (3) OZONOLYSIS

Benzene reacts with ozone and gives glyoxal. First of all triozonide is produced as an intermediate



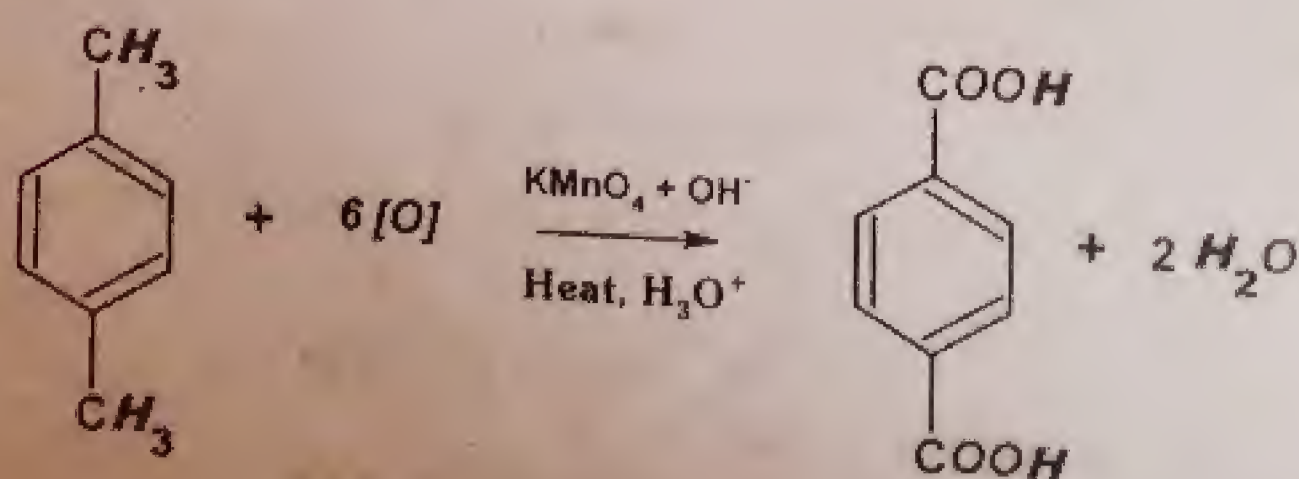
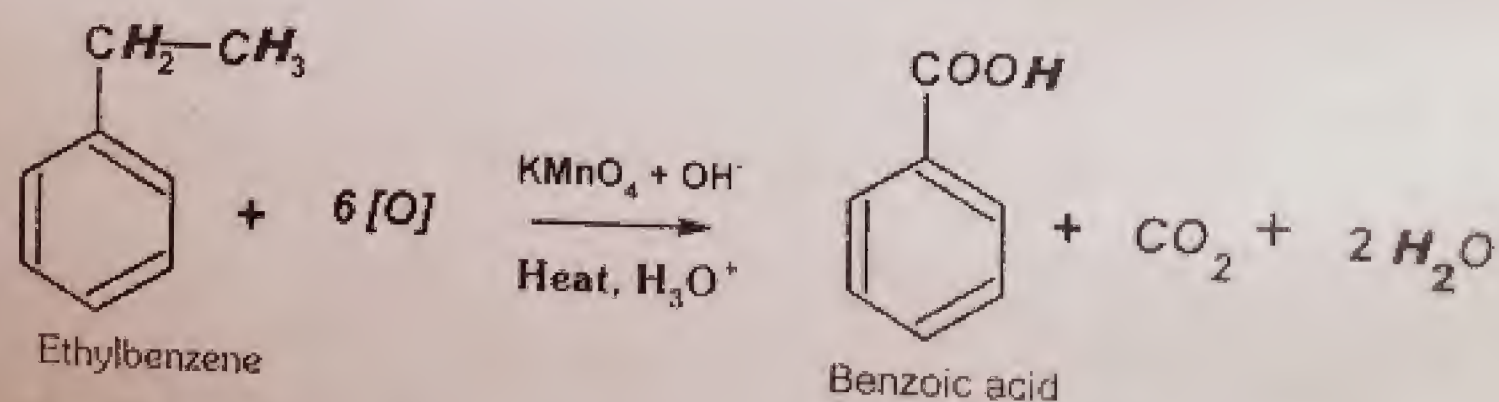
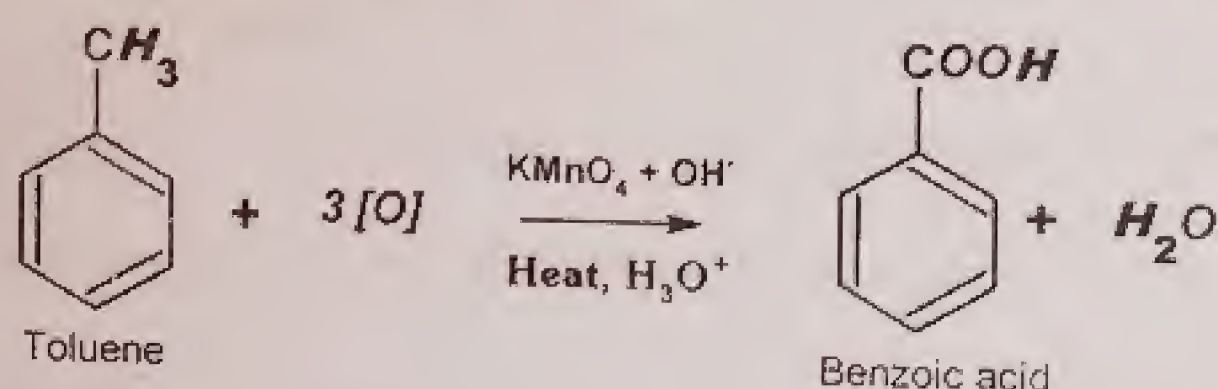
## (4) OXIDATION OF SIDE CHAIN

Alkyl groups present in the benzene ring are oxidized into carboxylic groups. The oxidizing agents are:

(i)  $\text{KMnO}_4 + \text{H}_2\text{SO}_4$

(ii)  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$

(iii) Dil.  $\text{HNO}_3$



### Conclusion:

When both methyl groups are oxidized and benzene ring remains unaffected, then it means that benzene ring is stable towards oxidizing agents.



## C) ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS

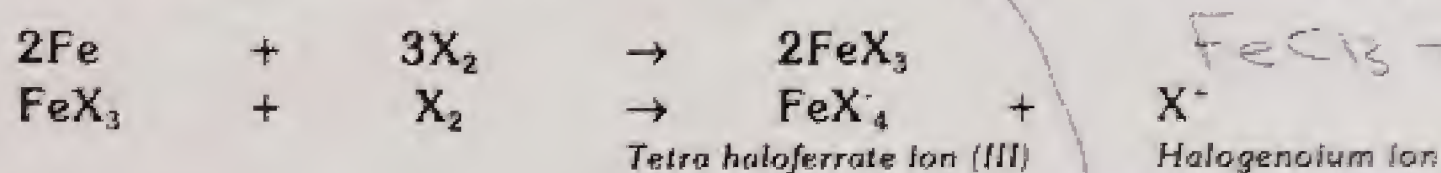
### General Introduction

The pi-electrons of benzene are highly stabilized due to resonance. They are not readily available for the electrophilic attack like the electros of alkenes. They do not assist in the attack of weak electrophiles. Hence more powerful electrophiles are required for a successful attack to penetrate and break the continuous sheath of electron cloud in benzene.

### Explanation and Example

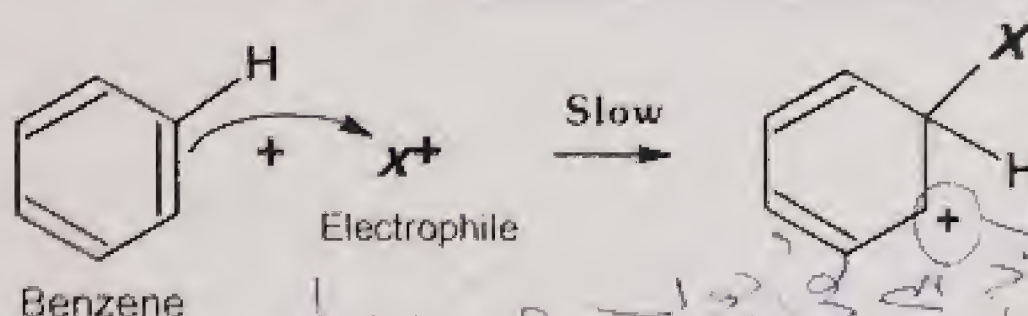
Substitution of halogen in benzene requires iron or corresponding ferric halide as catalyst. It reacts with halogen molecule to produce a powerful electrophile:

#### (i) Formation of a strong electrophile ( $X^+$ )

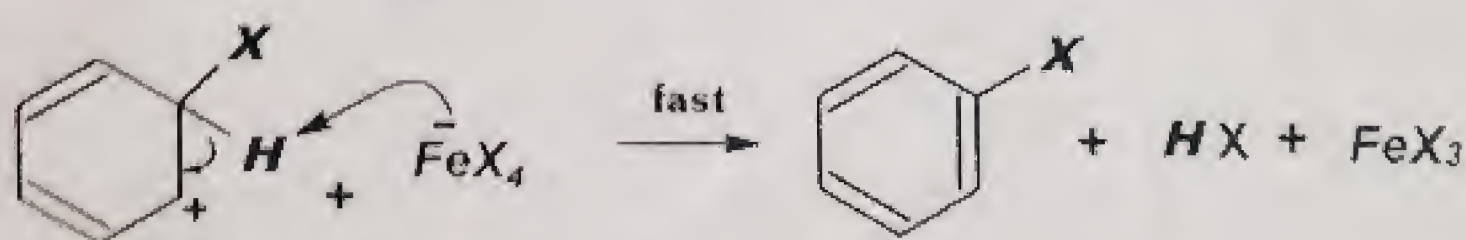


#### (ii) Attack of electrophile at pi-bond:

- The halogenation ion thus produced attacks as a powerful electrophile on the electrons of benzene ring

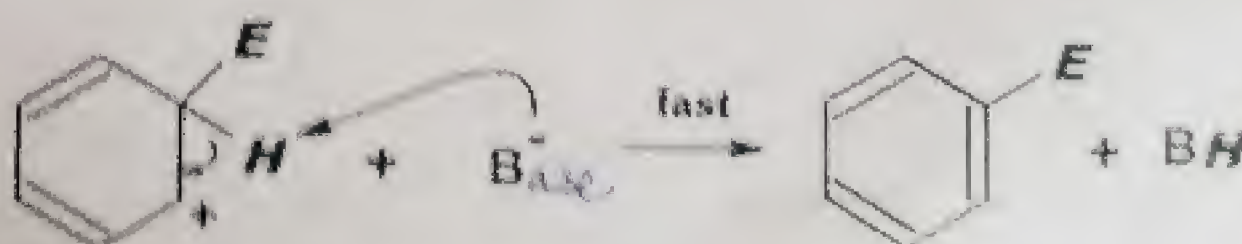
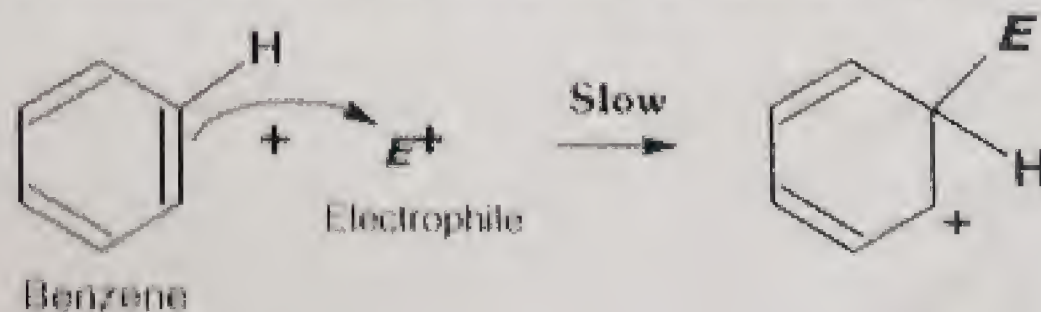


- It had benzene unstable. The stability is retained by the removal of H-atom to give substitution product.



### General Pattern of Substitution


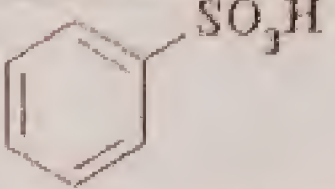
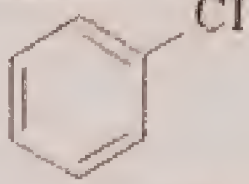
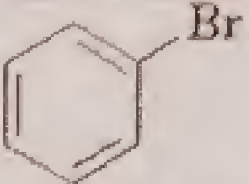

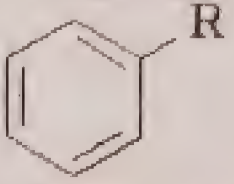
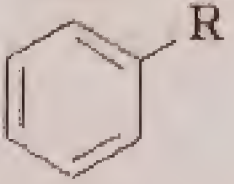
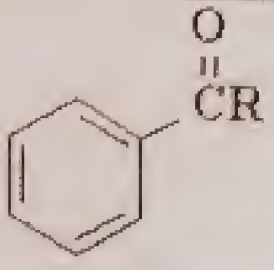
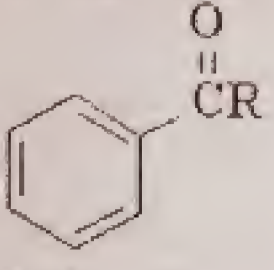
The general pattern of the chemical reactivity of benzene towards electrophiles can be shown as follows.



Substitution is preferred over addition in order to preserve the stable aromatic character



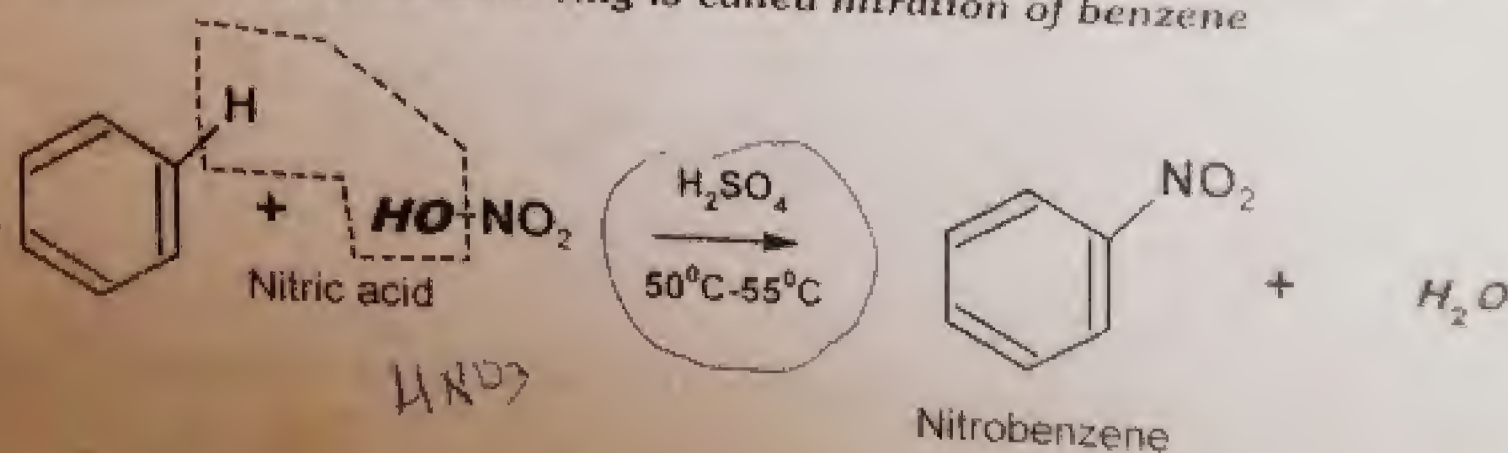
Summary

Reaction	Reagents	Electrophile	Product	Comments
Nitration	$\text{HNO}_3 / \text{H}_2\text{SO}_4$	$\text{NO}_2^+$		$\text{E}^+$ formed by loss of water from nitric acid
Sulfonation	$\text{H}_2\text{SO}_4$ or $\text{SO}_3 / \text{H}_2\text{SO}_4$	$\text{SO}_3$		Reversible
Halogenation	$\text{Cl}_2 / \text{Fe}$ or $\text{FeCl}_3$	$\text{Cl}^+$		$\text{E}^+$ formed by Lewis acid removing Cl
	$\text{Br}_2 / \text{Fe}$ or $\text{FeBr}_3$	$\text{Br}^+$		$\text{E}^+$ formed by Lewis acid removing Br
Alkylation	$\text{R-Cl} / \text{AlCl}_3$	$\text{R}^+$		$\text{E}^+$ formed by Lewis acid removing Cl
	$\text{R-OH} / \text{H}^+$ (See Page 298 for carbocation generation)	$\text{R}^+$		$\text{E}^+$ formed by loss of water from alcohol
	$\text{C=C} / \text{H}^+$ (See Page 148 for carbocation generation)	$\text{R}^+$		$\text{E}^+$ formed by protonation of alkene
Acylation	$\text{RCOCl} / \text{AlCl}_3$	$\text{RCO}^+$		$\text{E}^+$ formed by Lewis acid removing Cl
	$\text{RCO}_2\text{COR} / \text{AlCl}_3$	$\text{RCO}^+$		$\text{E}^+$ formed by Lewis acid removing $\text{RCO}$

Exercise Q3 (vi) Explain the following electrophilic substitution reactions of benzene with mechanism.  
(b) Nitration

(1) NITRATION

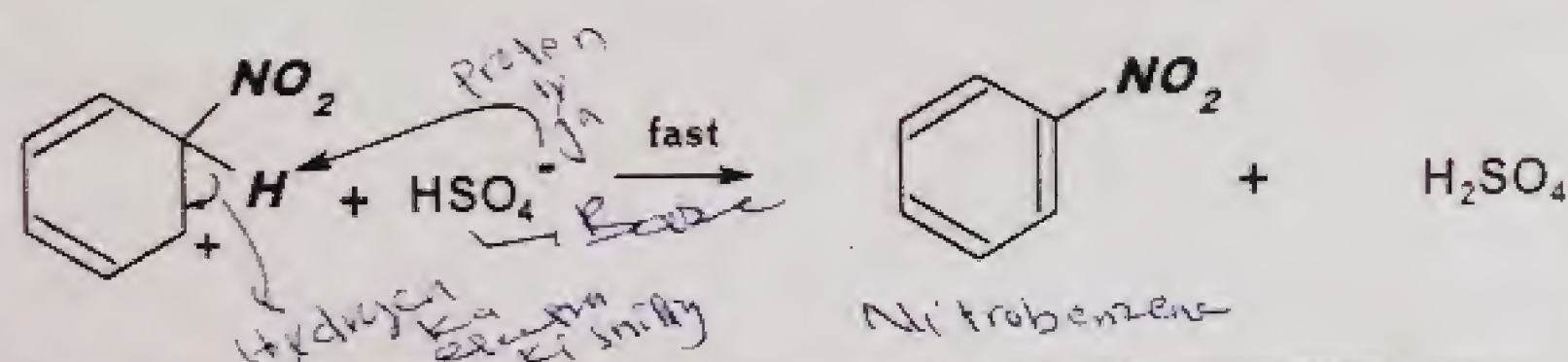
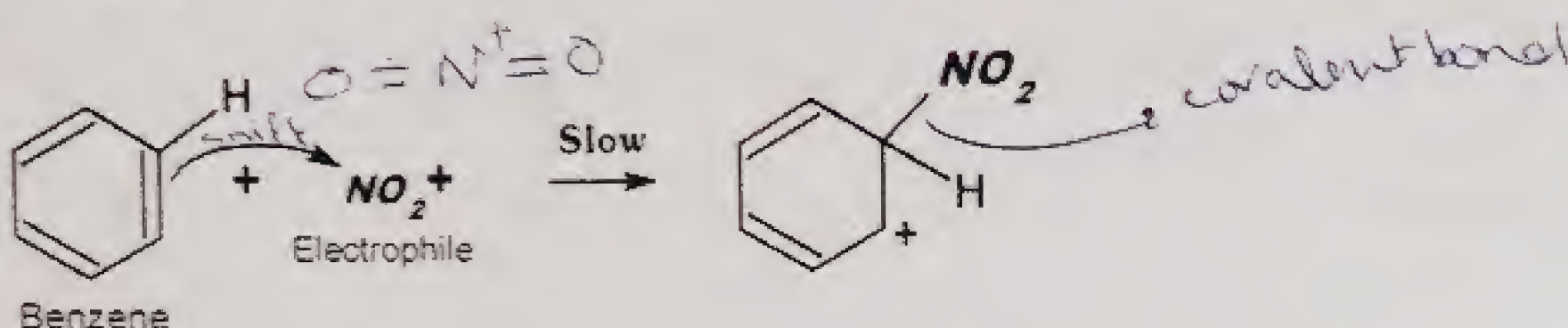
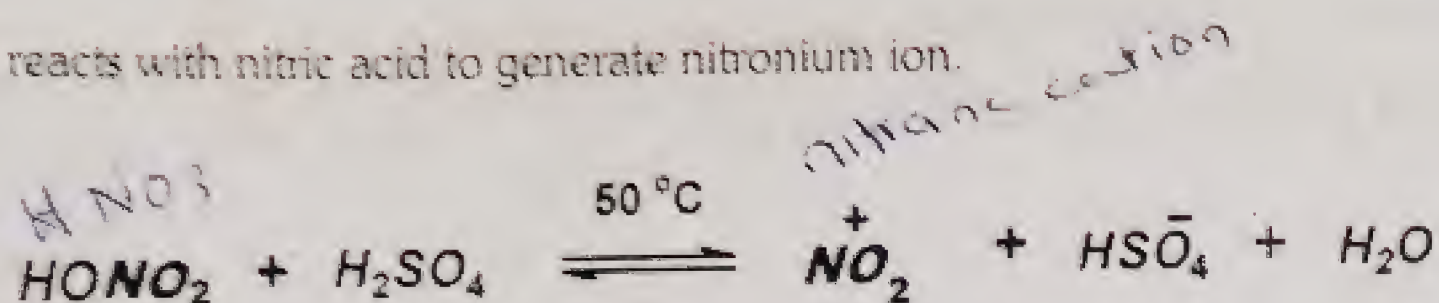
The introduction of nitro group in benzene ring is called nitration of benzene





### Mechanism

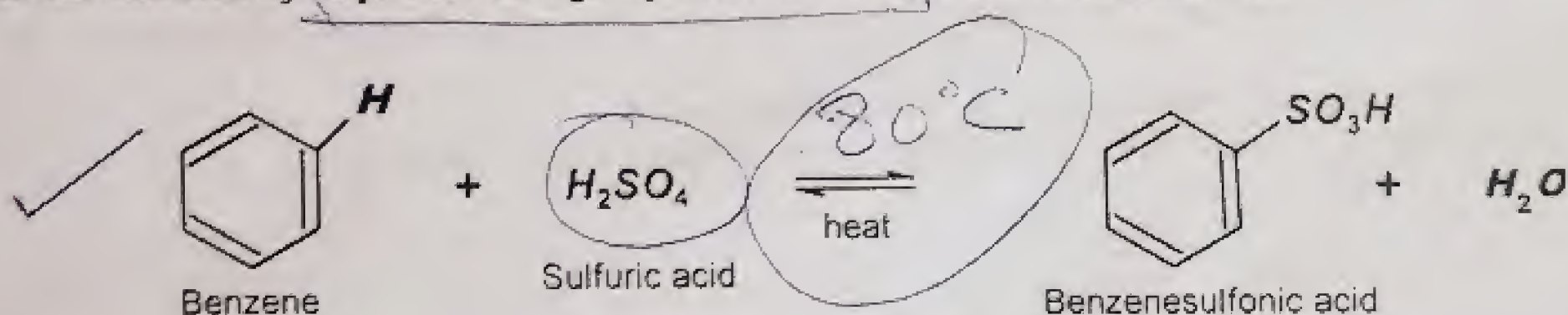
Sulphuric acid reacts with nitric acid to generate nitronium ion.



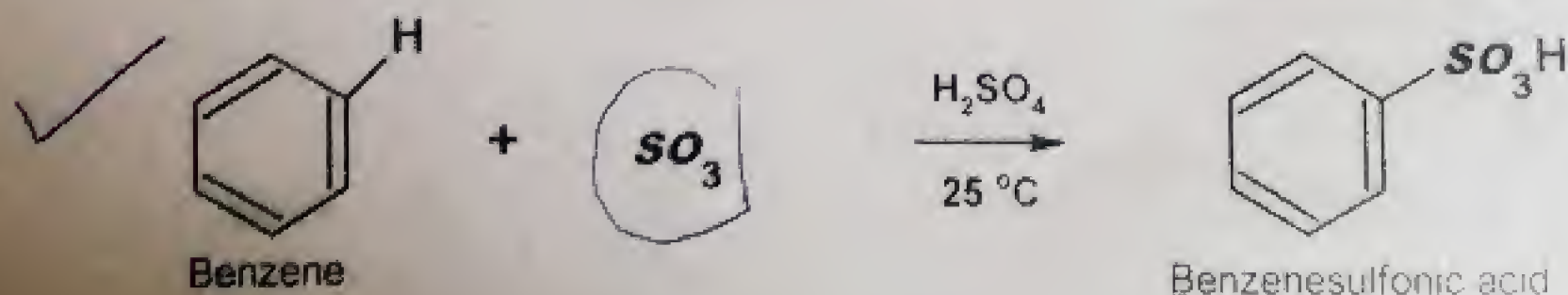
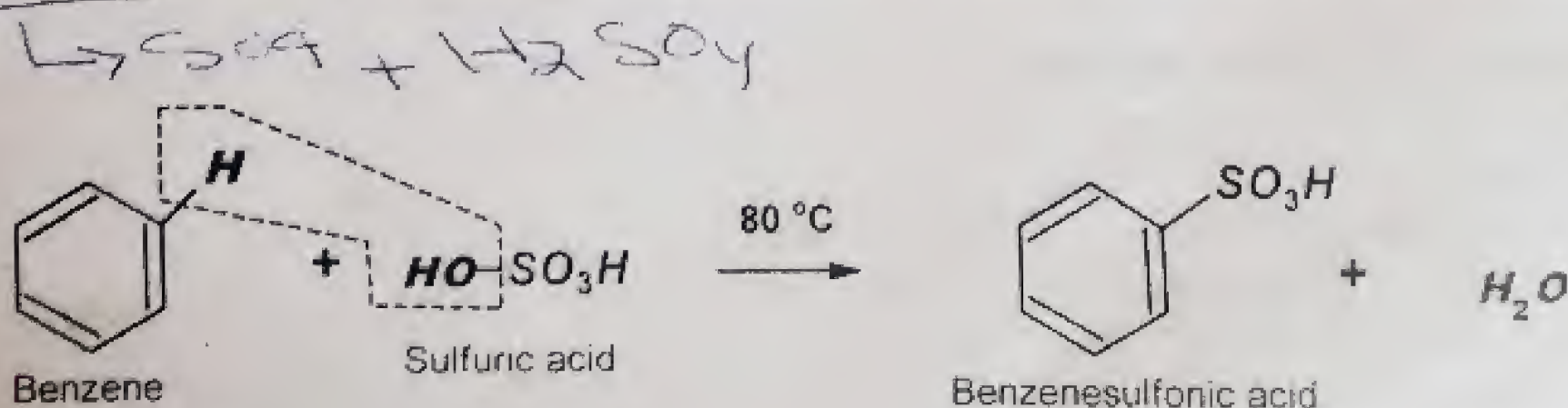
**Exercise Q3 (vi)** Explain the following electrophilic substitution reactions of benzene with mechanism.  
(c) Sulphonation.

### (2) SULFONATION

The introduction of sulphonic acid group in benzene ring is called Sulphonation.



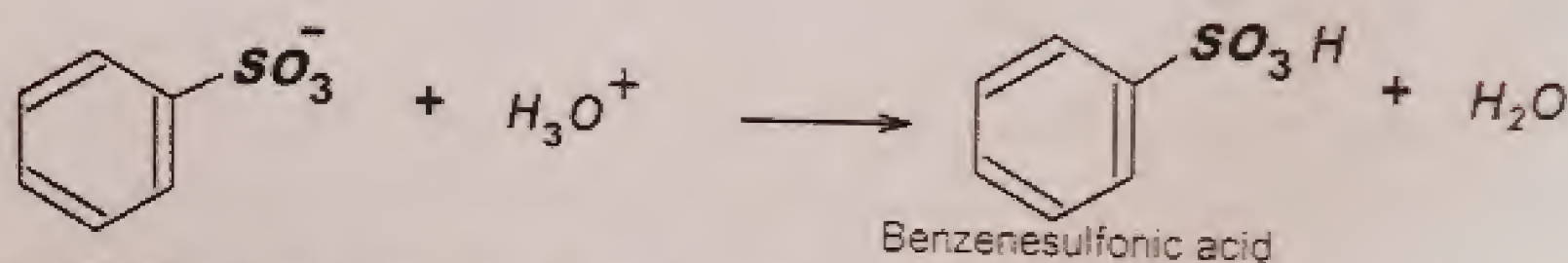
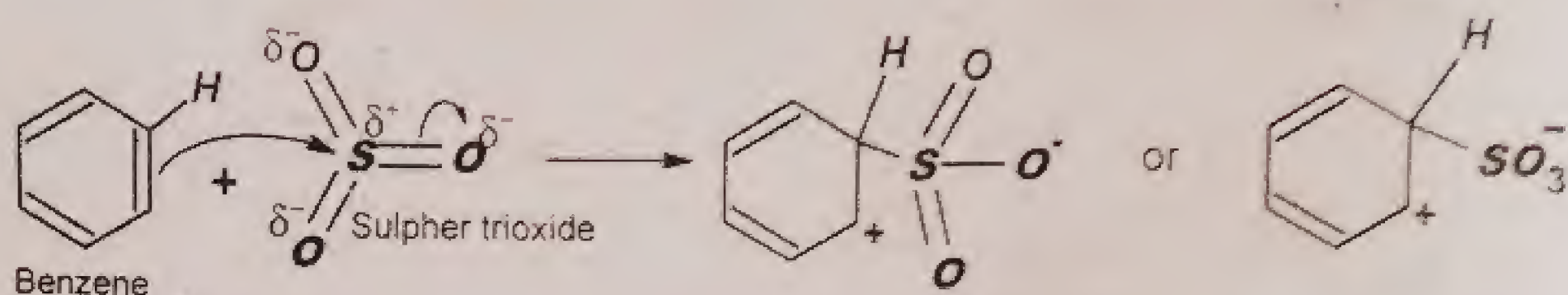
- When benzene is heated with fuming  $\text{H}_2\text{SO}_4$  or concentrated  $\text{H}_2\text{SO}_4$  it yields benzene sulphonic acid.
- Fuming  $\text{H}_2\text{SO}_4$  has free sulphur trioxide which is electron deficient (electrophile) and causes substitution.





**Mechanism:**

When sulphuric acid alone is used, the actual electrophile in this reaction is  $\text{SO}_3$

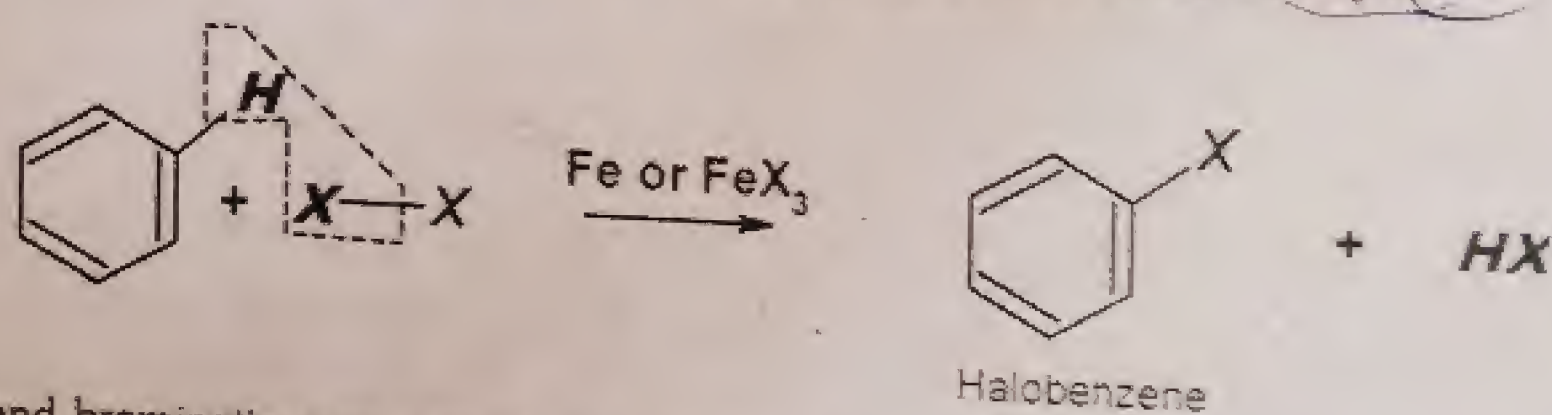


**Exercise Q3 (6)** Explain the following electrophilic substitution reactions of benzene with mechanism.  
(a) Halogenation

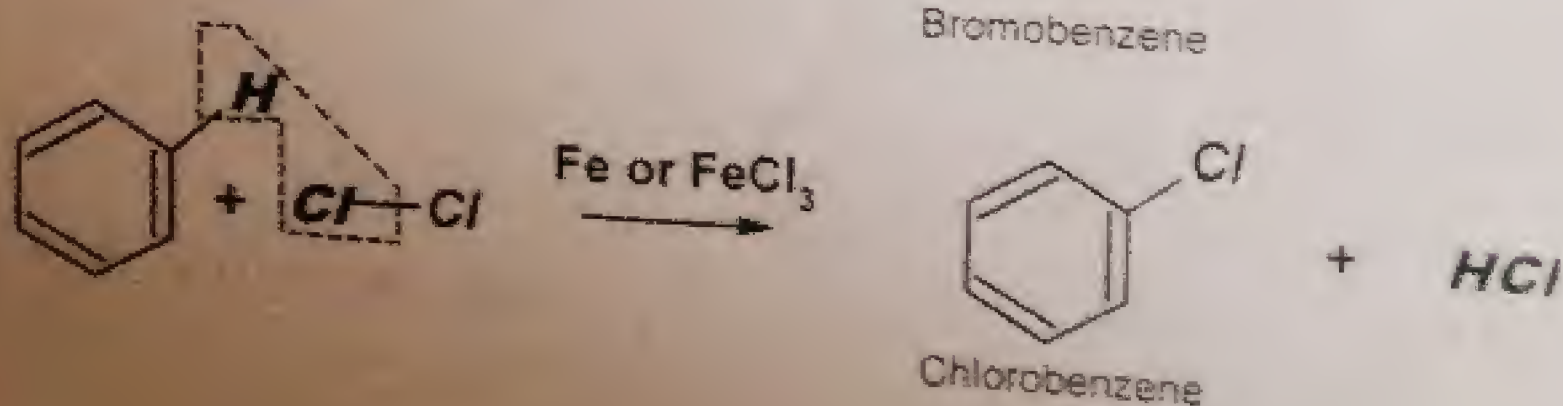
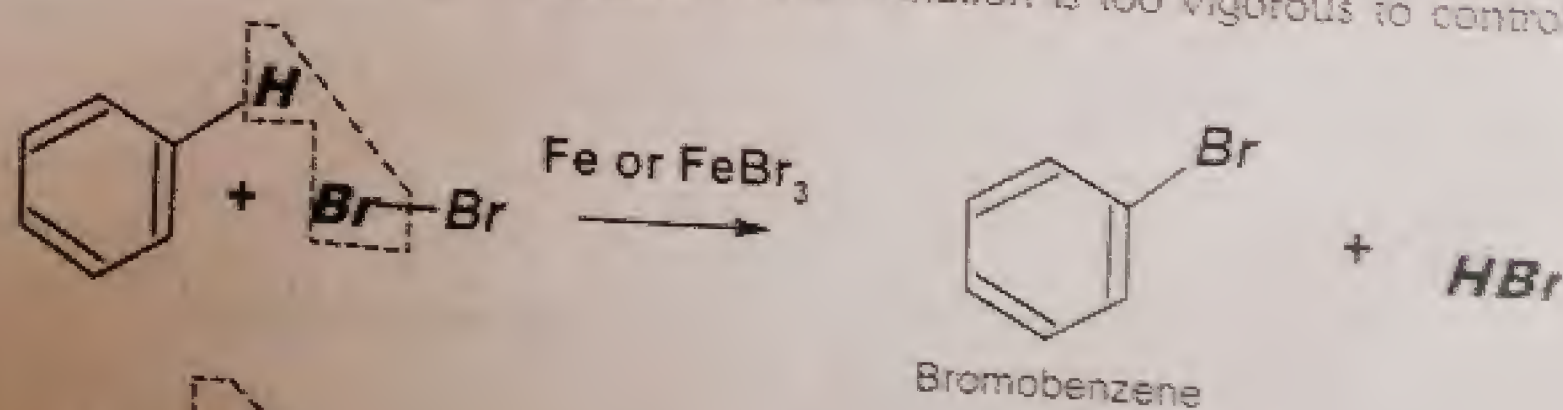
**HALOGENATION**

The introduction of halogen in benzene ring is called halogenation.

Halogenation of benzene occurs with halogens (X) in the presence of a catalyst  $\text{FeX}_3$  or Fe.



Chlorination and bromination are normal reaction but fluorination is too vigorous to control. Iodination gives poor yield.



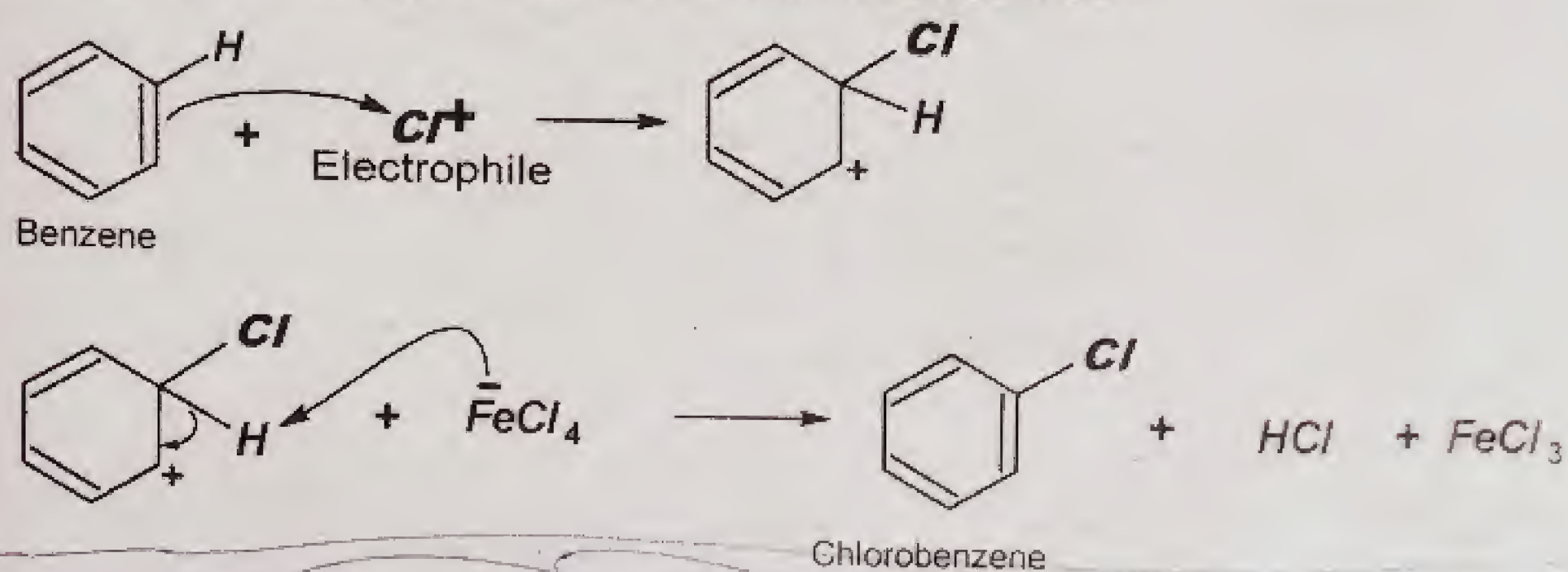


**Mechanism:**

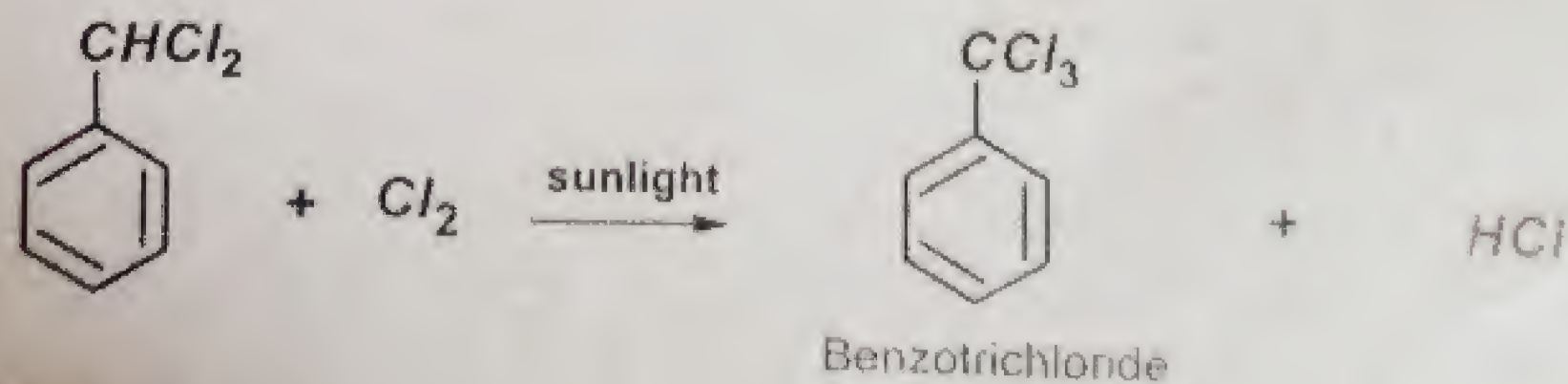
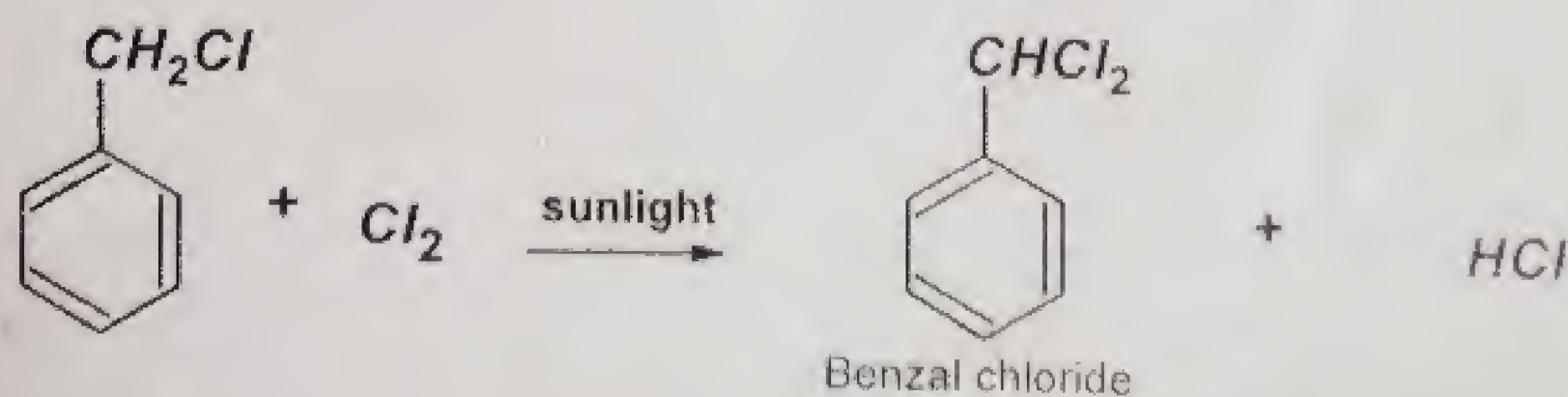
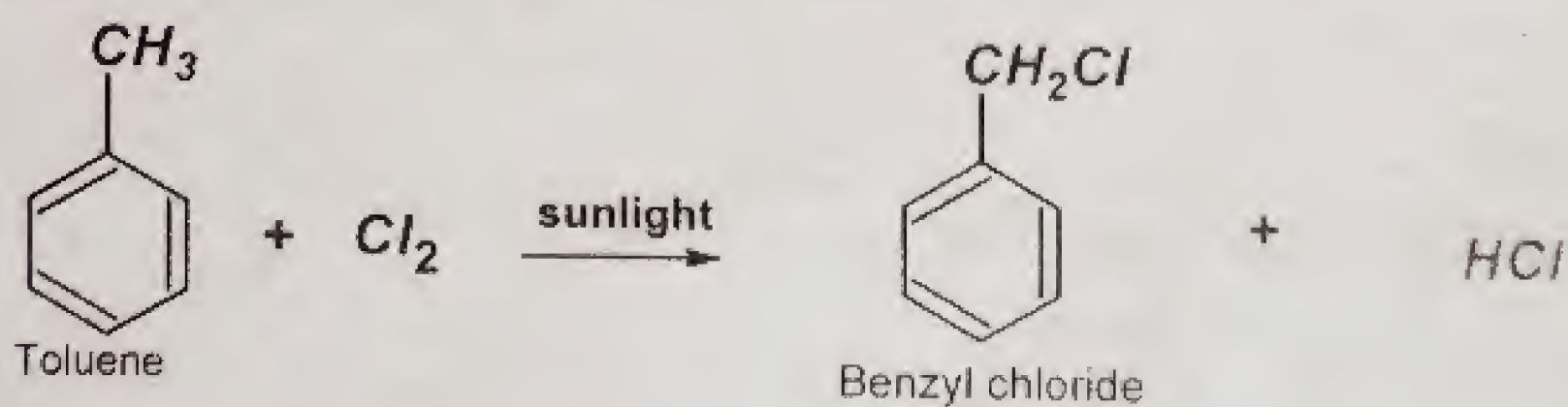
The actual halogenation agent is  $X^+$  that is formed by the following mechanism



The  $Cl^+$  being a strong electrophile is ready for successful attack on benzene.



When alkyl benzenes are treated with chlorine or bromination the presence of sunlight, only the alkyl groups are substituted.

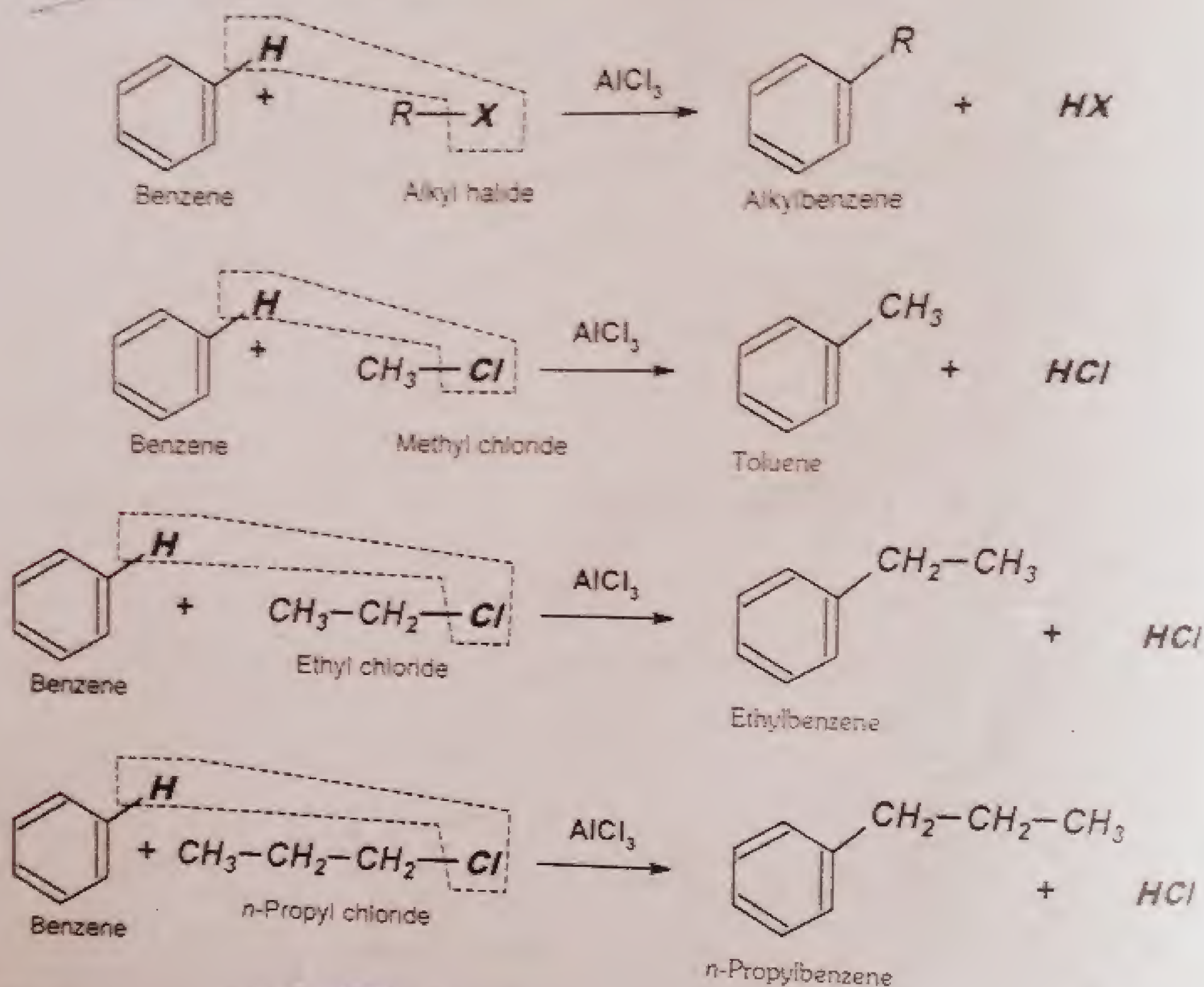




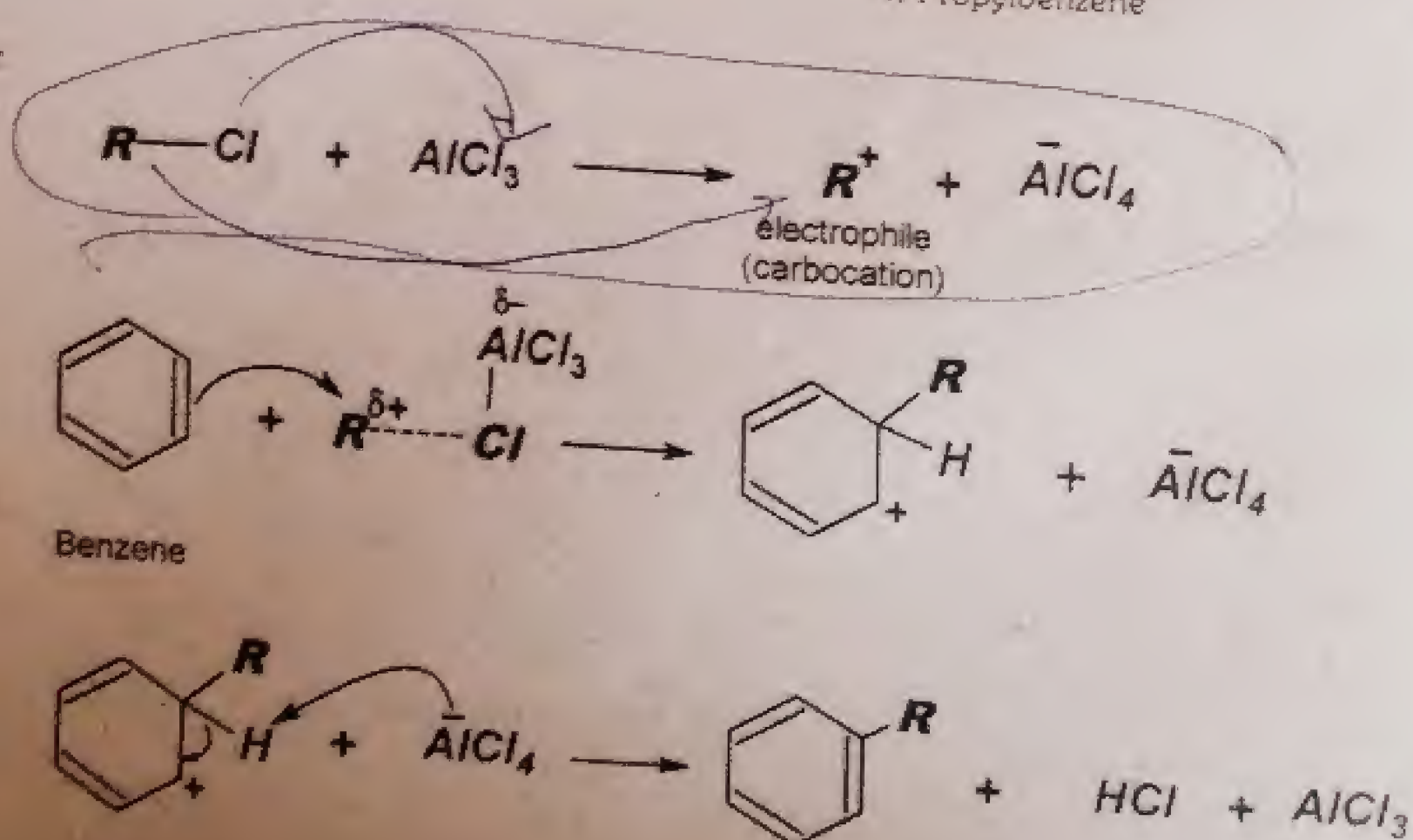
**Exercise Q3 (5)** Explain Friedel Craft acylation and alkylation with complete mechanism.

### FRIEDEL-CRAFTS ALKYLATION

The introduction of an alkyl group in the benzene ring in the presence of an alkyl halide and a catalyst is called Friedel Crafts alkylation or Alkylation.



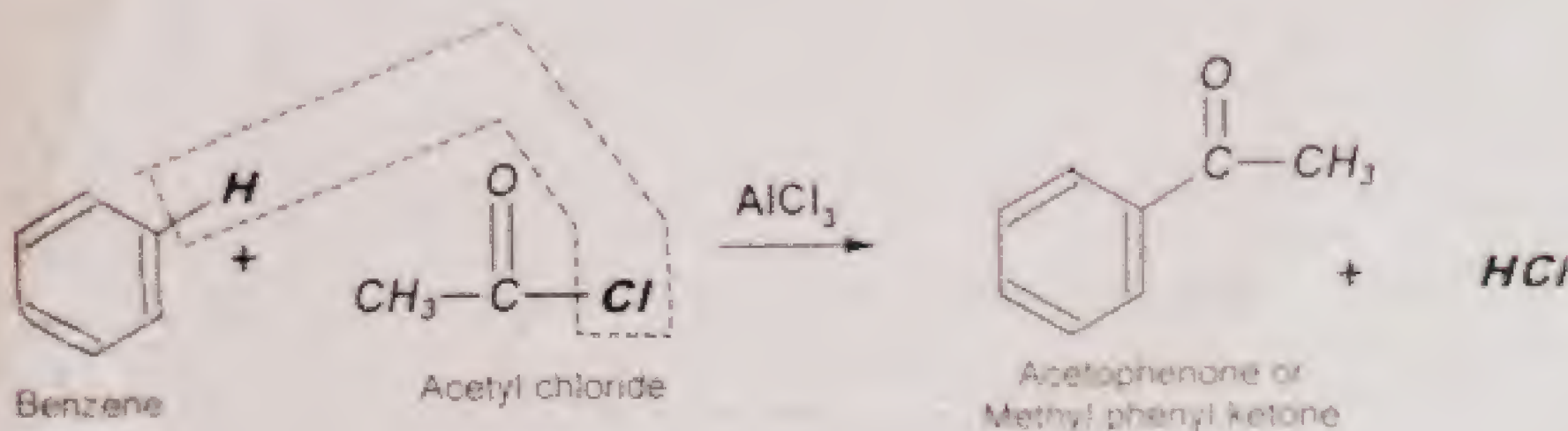
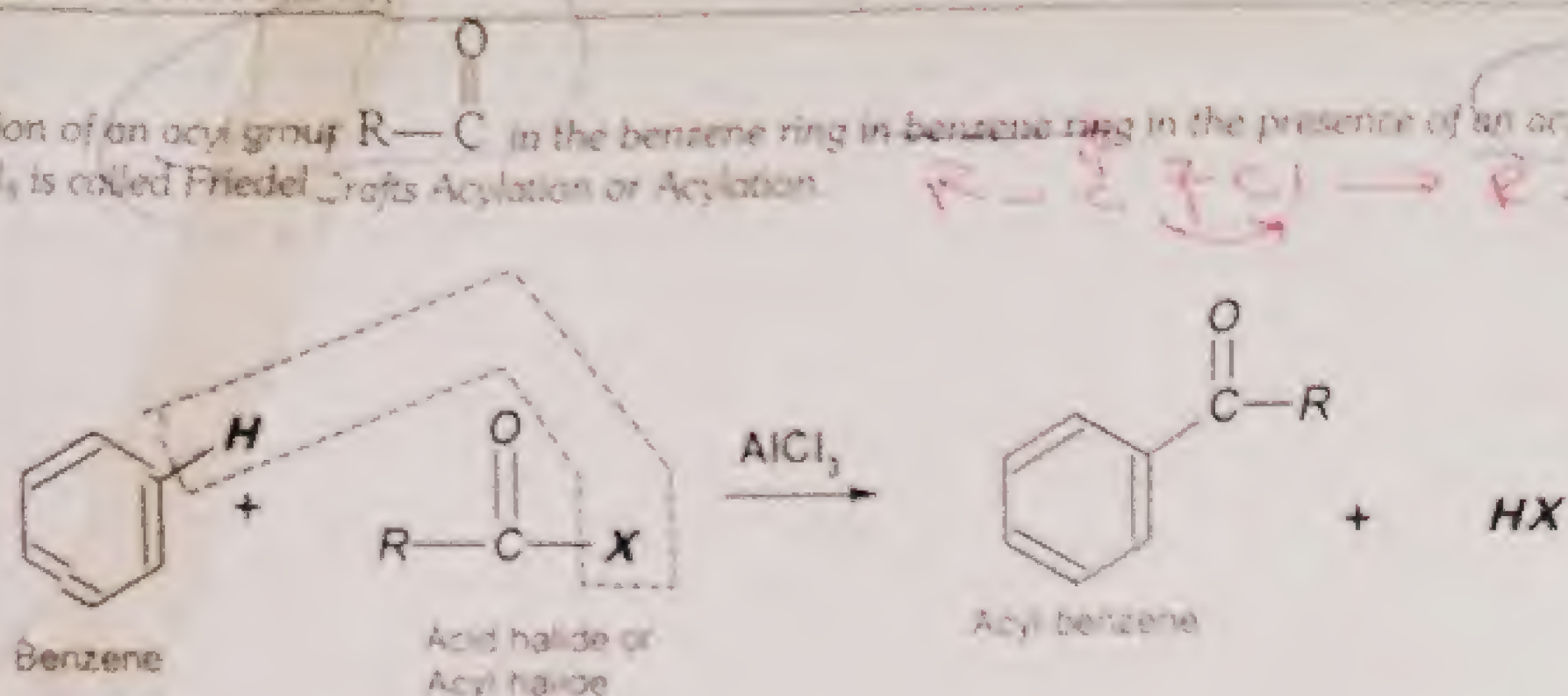
#### Mechanism:



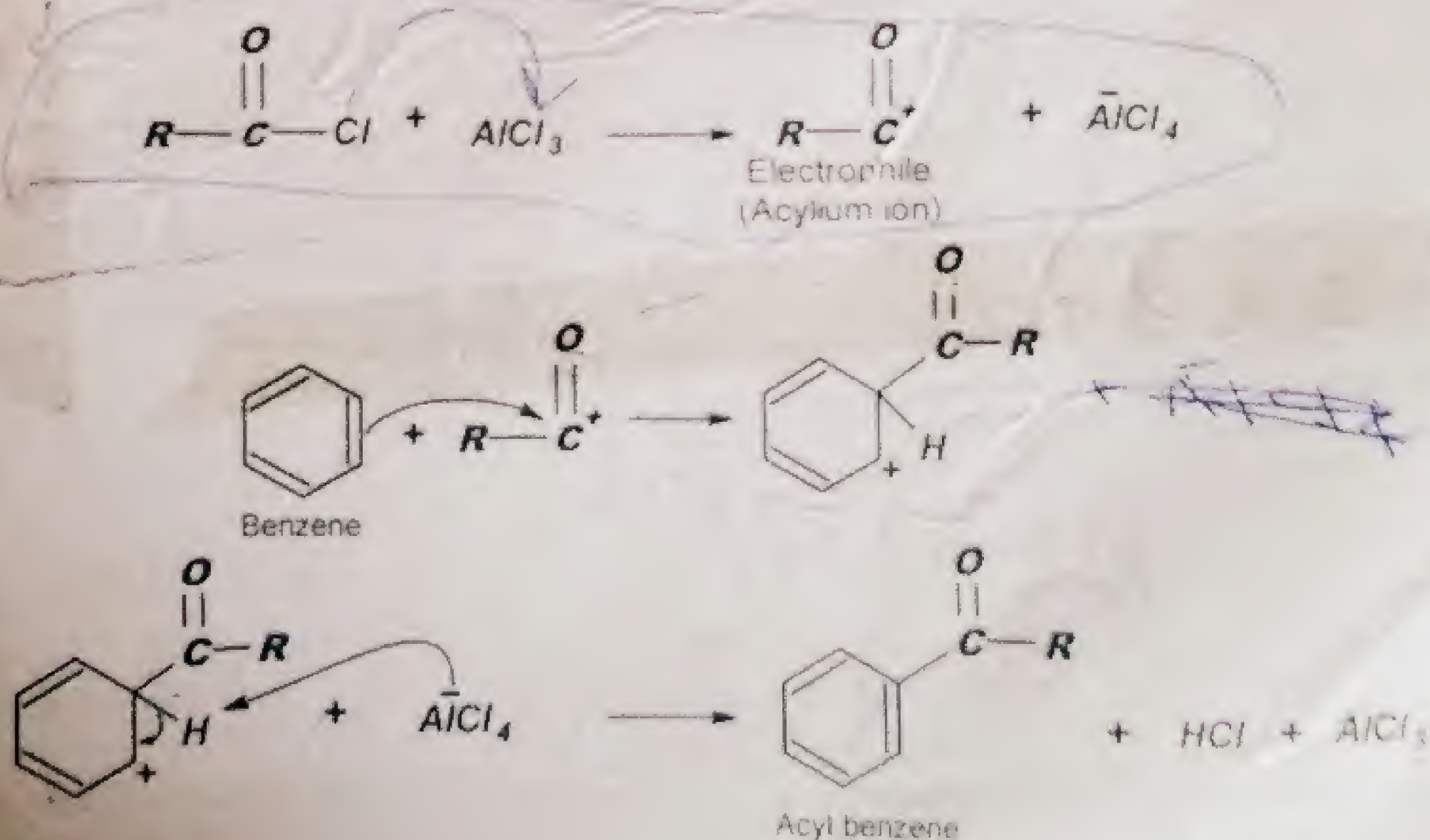


## RIEDEL-CRAFTS ACYLATION

The introduction of an acyl group  $R-\overset{\overset{O}{\parallel}}{C}$  in the benzene ring in the presence of an acyl halide and catalyst  $AlCl_3$  is called Friedel Crafts Acylation or Acylation.



### Mechanism

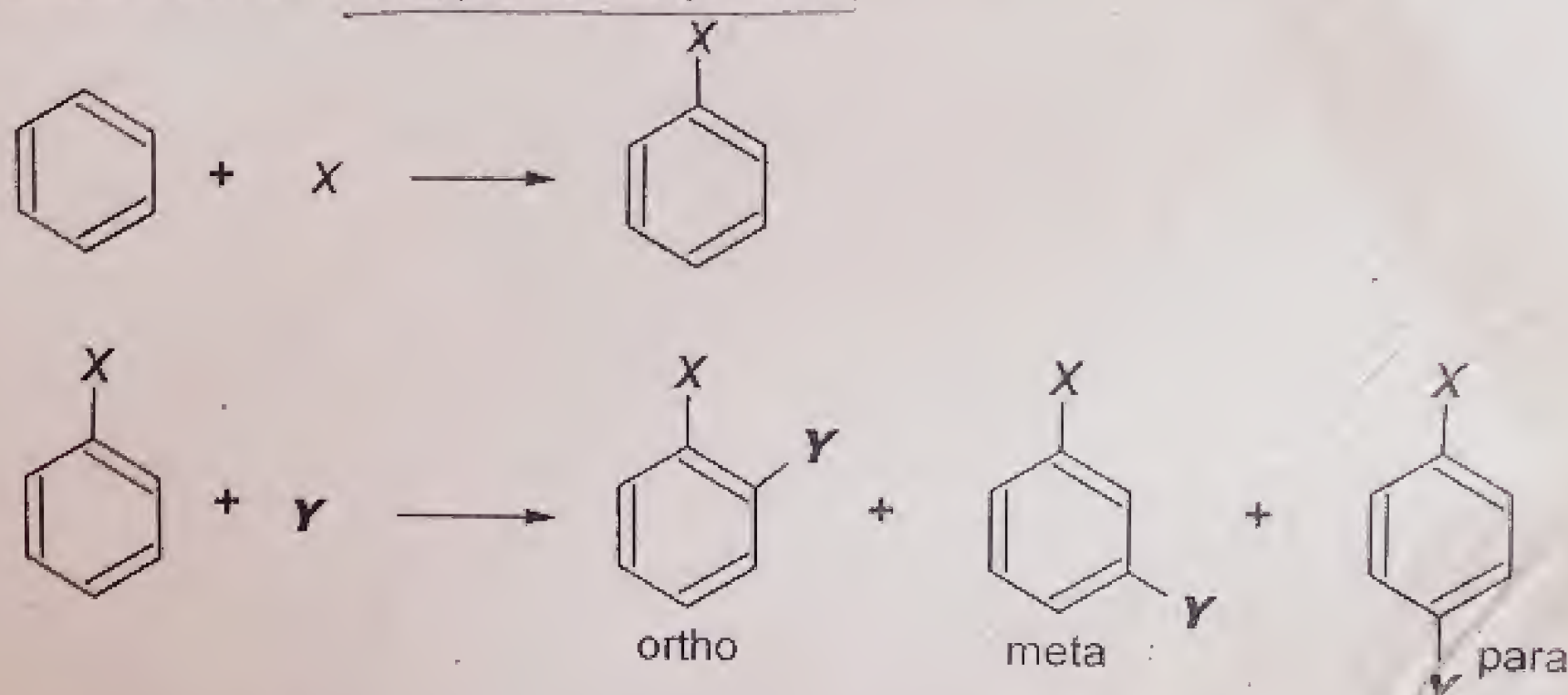




## SUBSTITUENT EFFECTS

### (Table of Substituent Effects) and Making Poly-substituted Benzenes

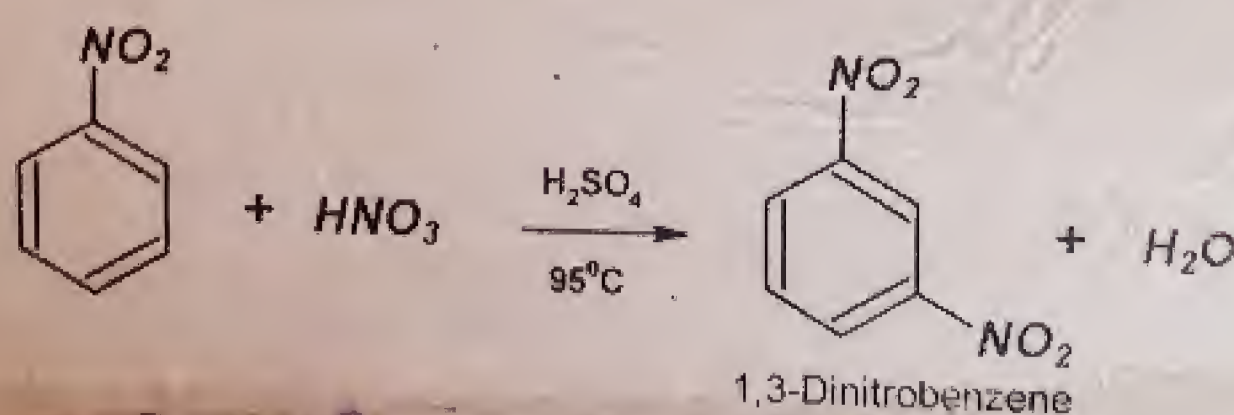
- When an electrophilic substitution reaction takes place on benzene ring, we get only one monosubstituted benzene because all the six positions in the ring are equivalent.
- However, the position of a second group into the ring depends on the nature of the first group. The second substituted group enters in ortho, para or meta position.



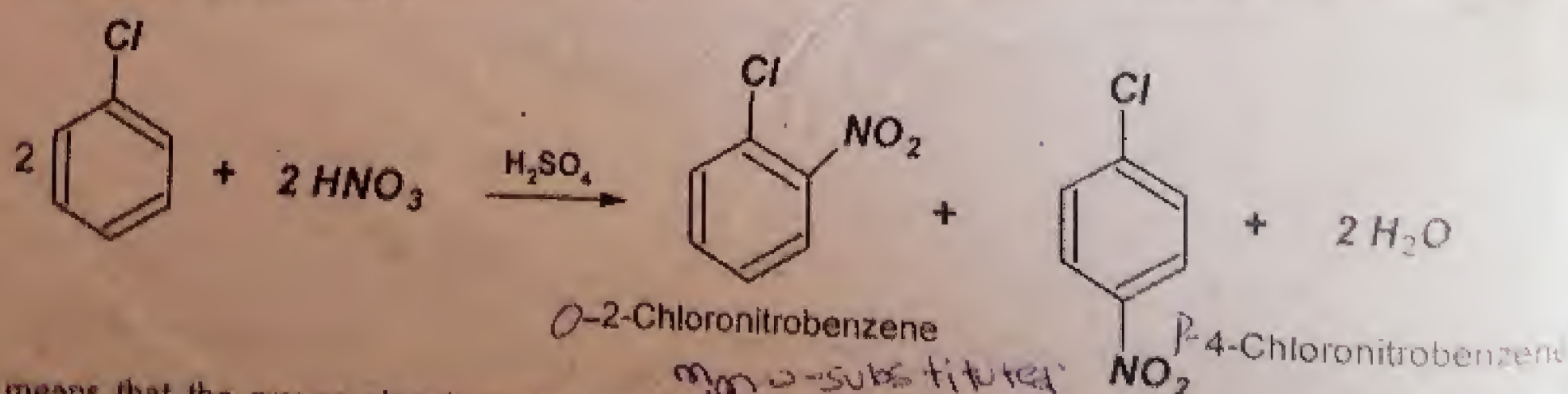
- On chance basis 40% ortho (20% + 20%), 40% meta (20% + 20%) and 20% para disubstituted products are expected.
- However, the results do not agree with chance substitution ratio.

#### Examples

(i) m-nitrochlorobenzene is the main product of the following halogenation reaction.



(ii) On the other hand, a mixture of 2-chloronitrobenzene and 4-chloronitrobenzene is obtained from the nitration of chlorobenzene.



It means that the groups already present in the benzene ring directs the second incoming group and determines its position.

There are two types of groups:

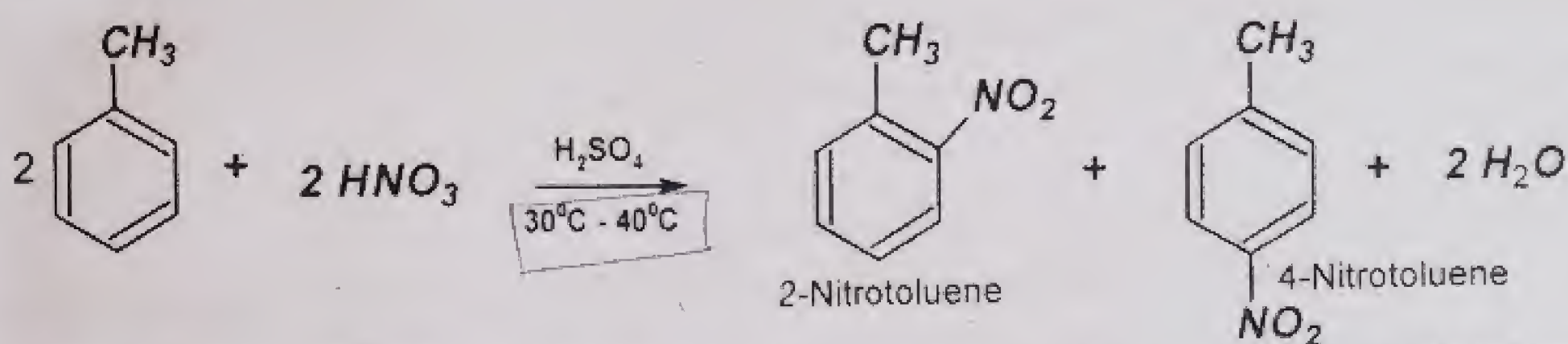
- (1) ortho- and para-directing groups
- (2) meta-directing groups



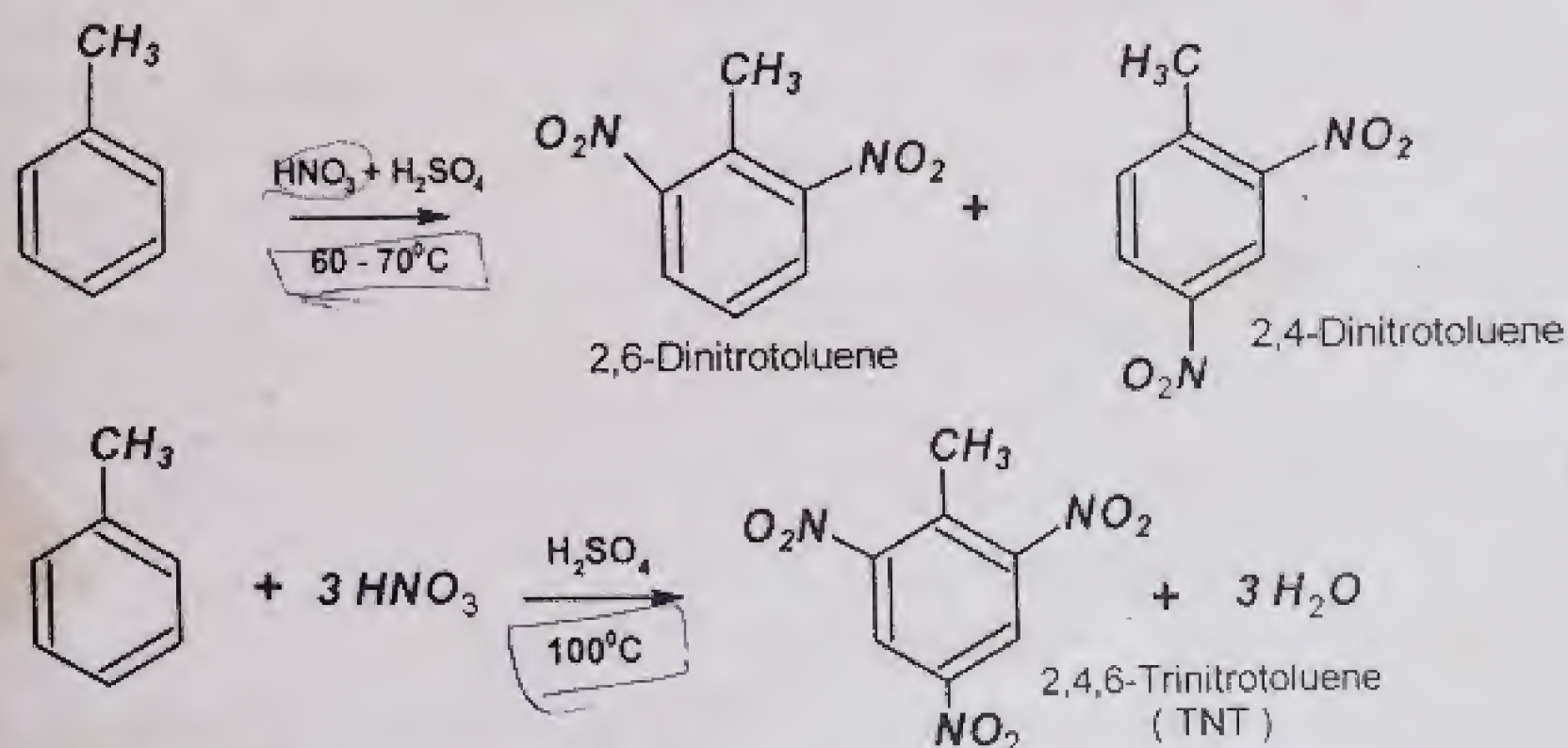
## ORTHODIRECTING GROUPS

These groups release electrons towards the benzene ring, at *ortho* and *para* positions. Because these positions are richer in electron for attack of an electrophile. The second group is substituted at *ortho* and *para* positions. They generally increase the reactivity of benzene ring except halogens.

Example:



The electron releasing effect of methyl groups is significant and it makes the ring a good nucleophile. Due to this increased reactivity, more nitro groups can enter the ring.

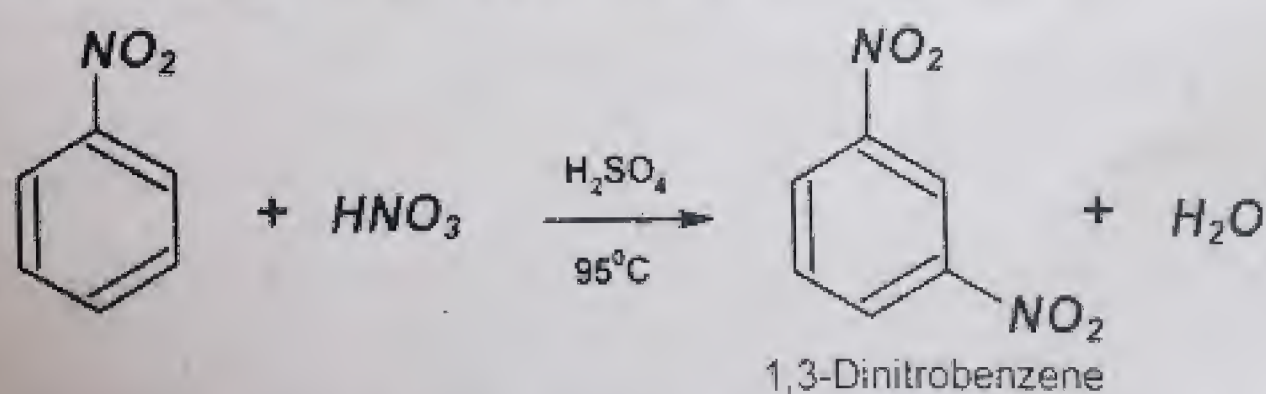


Examples (ortho- and para- directing groups)

$-\text{N}(\text{CH}_3)_2$ ,  $-\text{NH}_2$ ,  $-\text{OH}$ ,  $-\text{OR}$ ,  $-\text{OCH}_3$ ,  $-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{I}$

## METADIRECTING GROUPS

These groups withdraw the electrons of the benzene ring from *ortho* and *para* positions. Due to the electron withdrawing effect of such substituents, the *ortho* and *para* positions are more electron deficient than the *meta* position. Thus the incoming electrophile will prefer to attack on *meta* position rather than *ortho* and *para* positions. These groups are called *meta*-directing groups. These groups decrease the chemical reactivity of benzene.



The substitution of third nitro groups is not possible because nitro group has deactivated the ring.

Examples (meta-directing groups):

$-\text{NR}_3^+$ ,  $-\text{CN}$ ,  $-\text{COOH}$ ,  $-\text{CHO}$ ,  $-\text{COR}$



**RULE:**

If the electronegativity of the atom of the group attached to the benzene ring is greater than any atom of the group, the whole group will act as electron repelling and will increase the reactivity of benzene and direct the entrant to ortho, para positions. On the other hand  
 If the electronegativity of such atom is less, it will be under constraint and it will withdraw electron from the ring making it less reactive and directing the new entrant to meta position.

**Examples**

- (i)  $-\text{NH}_2$  Nitrogen with greater electronegativity from hydrogen.
- (ii)  $-\text{Cl}$  has no other atom hence will have no danger of pulling electrons. Thus it is electron repelling and  $p$ -directing group. Hence  $o$ - and  $p$ -directing.
- (iii)  $-\text{N}(\text{O})_2$  Nitrogen with less electronegativity from O. Hence  $m$ -directing.
- (iv) In  $-\text{SO}_3\text{H}$ , the electronegativity of oxygen is greater than that of S, hence oxygen disturbs substitution which in turn withdraws electrons from benzene ring hence  $m$ -directing.

**MAKING POLYSUBSTITUTED BENZENES**

Since the position of electrophilic attack on a substituted benzene ring is controlled by the substituent already present rather than the approaching electrophile, the order of events in the synthesis of polysubstituted benzene needs careful planning to ensure success.

The two factors that need to be monitored are:

- regiochemistry (region-selective means position on benzene ring)
- reactivity (for example Friedel-Crafts reactions are limited to halobenzenes and activated benzenes)

**QUICK QUIZ-7**

1. (a) Describe the structure of benzene on the basis of following

- (i) atomic orbital treatment Page 184
- (ii) resonance method Page 186

✓ (b) Prove that benzene has a cyclic structure. (Exercise Q3 (4): will you prove that benzene has cyclic structure? Benzene adds three hydrogen molecules which shows the presence of three double bonds. Molecular formula of benzene is  $\text{C}_6\text{H}_6$  which does not correspond to any alkene or alkyne. Hence, benzene should have a cyclic structure. Moreover, the product formed during hydrogenation is cyclohexane which is a cyclic compound.

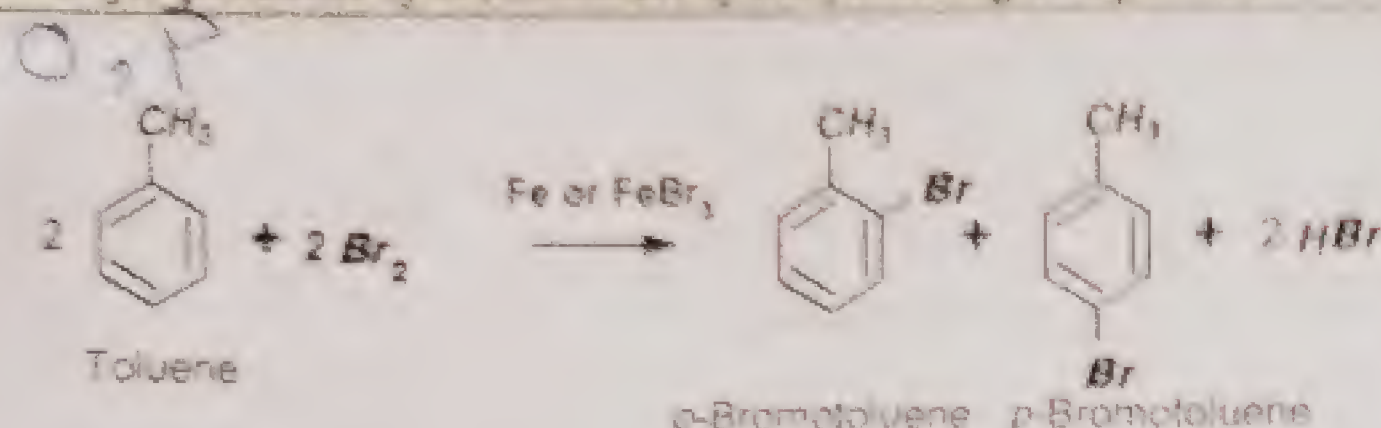
The cyclic structure was given by Kekulé and then confirmed by X-ray analysis. The structure of benzene is





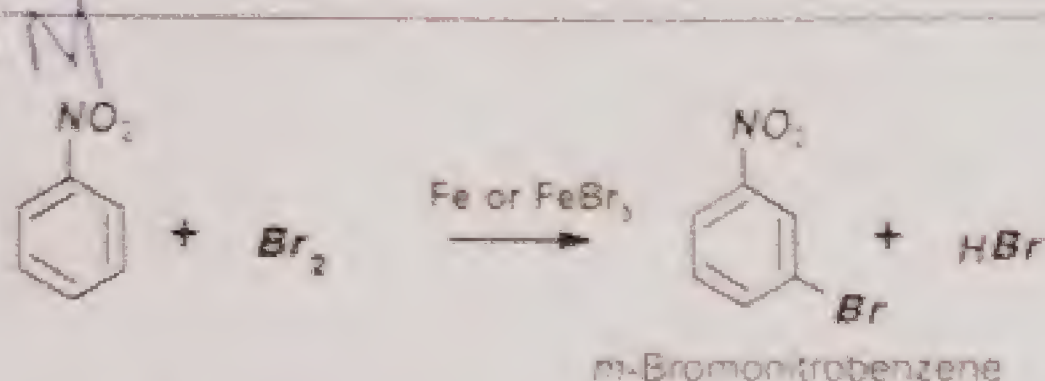
2. Predict the major products of bromination of the following compounds

(a) Toluene



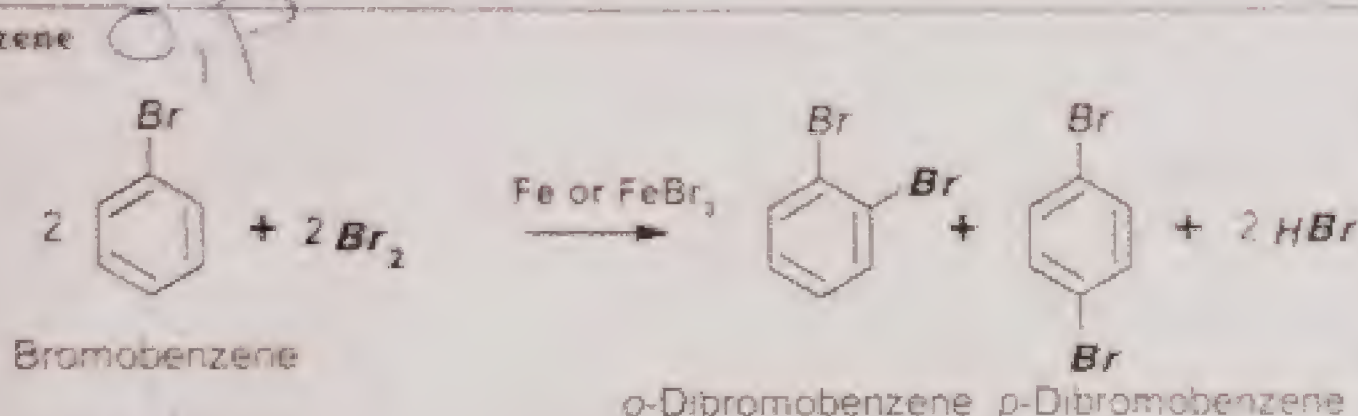
Since  $\text{CH}_3$  group on benzene ring is an o, p-director,  
So only o- and p-products are formed

(b) Nitrobenzene



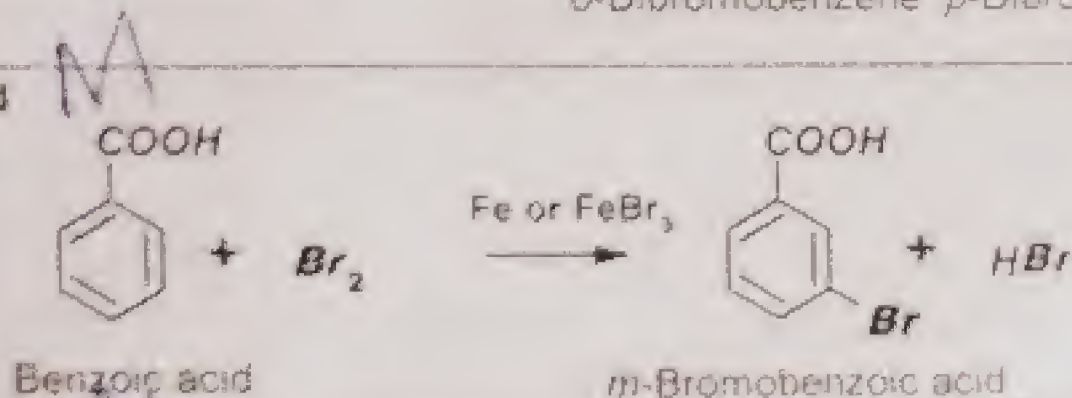
Since  $\text{NO}_2$  group on benzene ring is a m-director,  
So only m-product is formed

(c) Bromobenzene



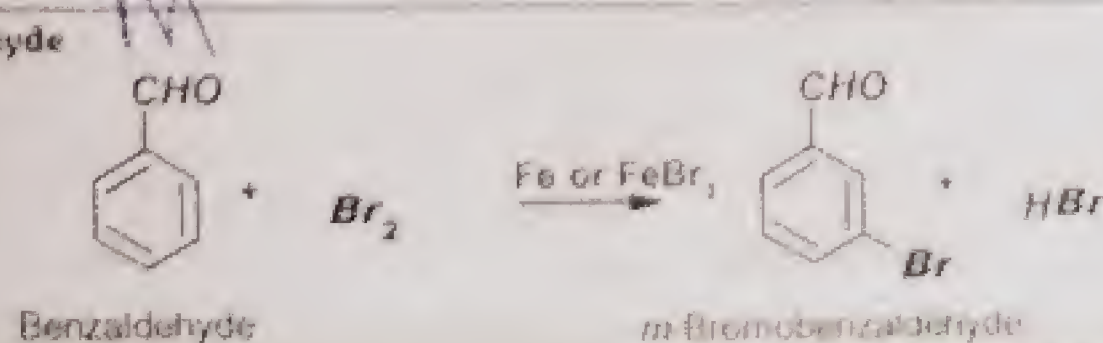
Since  $\text{Br}$  group on benzene ring is an o, p-director,  
So only o- and p-products are formed

(d) Benzoic acid



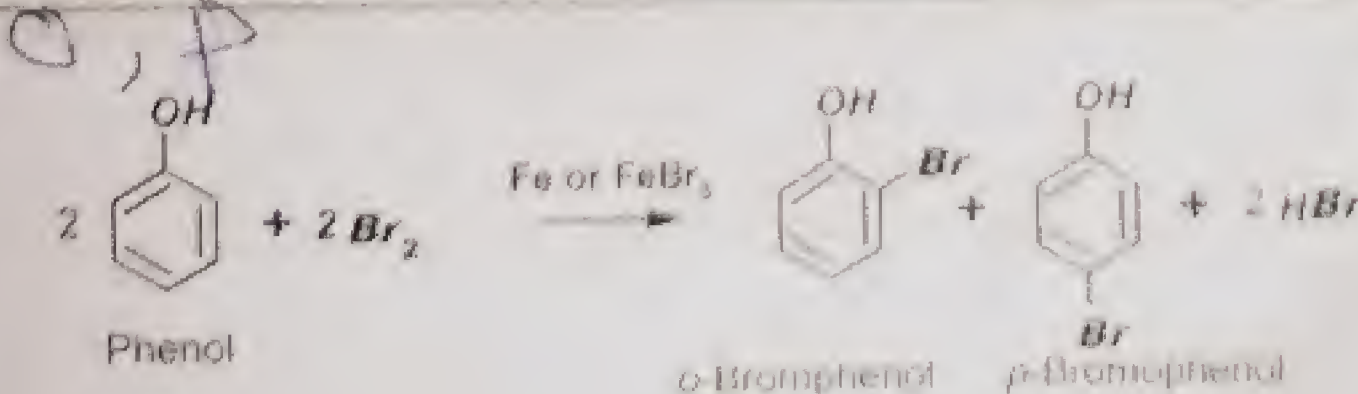
Since  $\text{COOH}$  group on benzene ring is a m-director,  
So only m-product is formed

(e) Benzaldehyde



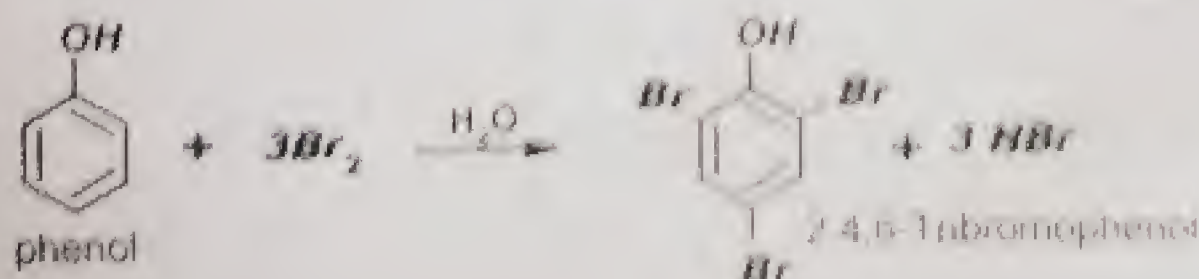
Since  $\text{CHO}$  group on benzene ring is a m-director,  
So only m-product is formed

(f) Phenol



Since  $\text{OH}$  group on benzene ring is an o, p-director,  
So only o- and p-products are formed

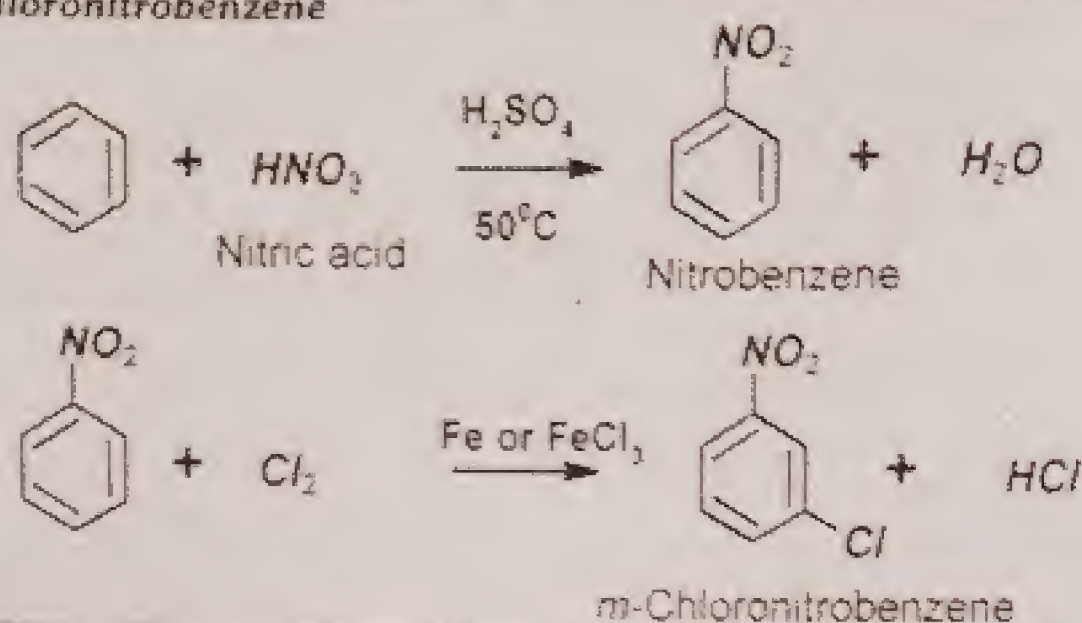
or



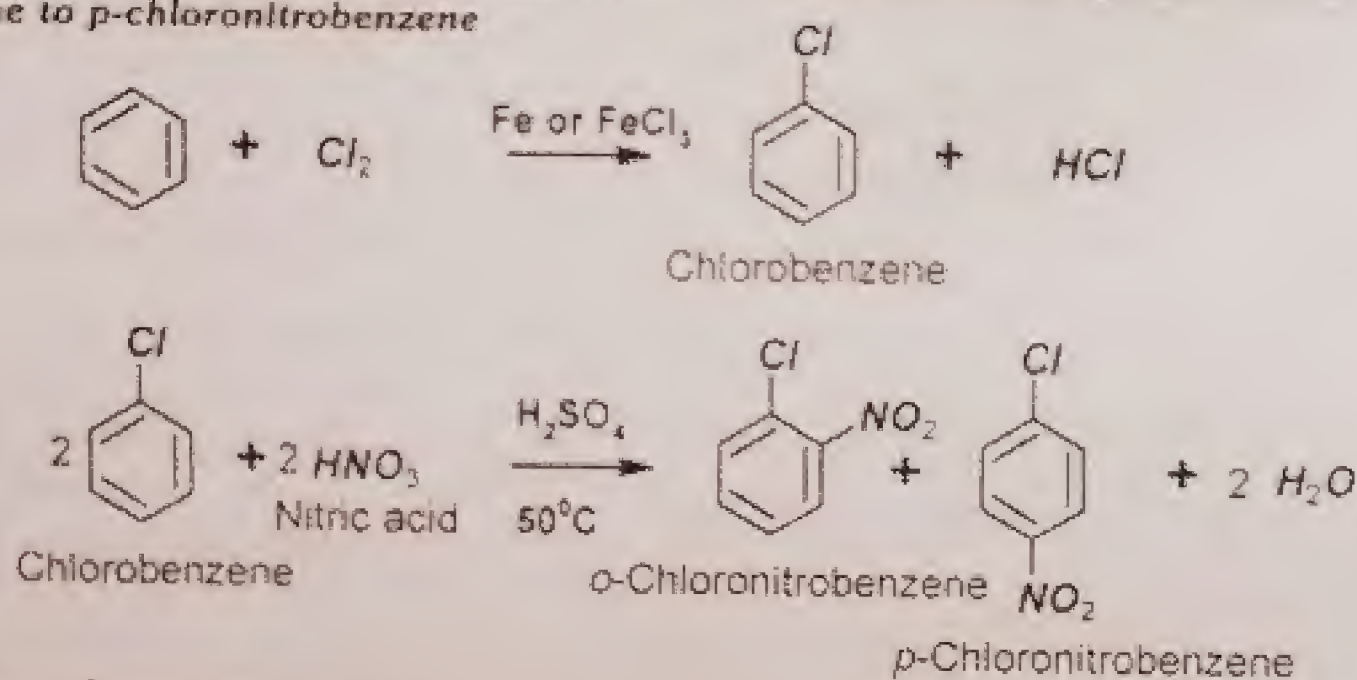


## SOME IMPORTANT CONVERSIONS

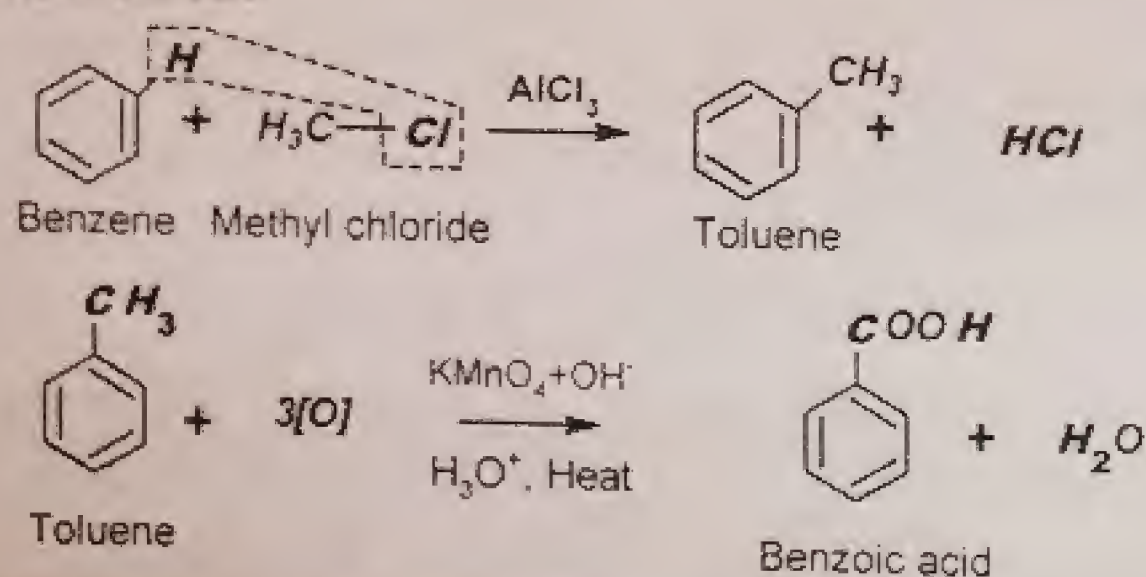
### (i) Benzene to m-chloronitrobenzene



### (ii) Benzene to p-chloronitrobenzene



### (iii) Benzene to Benzoic acid



## SOCIETY, TECHNOLOGY AND SCIENCE

### HYDROCARBONS IMPORTANT AS FUEL FOR FUTURE ENERGY NEEDS OF PAKISTAN

Ethanol, Natural Gas, Propane, Biodiesel - an alternative fuel based on vegetable oils or animal fats, Methanol - also known as wood alcohol, P-Series fuels - a blend of ethanol, natural gas liquids and methyltetrahydrofuran (MeTHF). P-Series fuels can be used alone or mixed with gasoline in any ratio by simply adding it to the tank.

### USES OF HYDROCARBONS

- (1) Butane is used as a fuel in lighter.
- (2) Butane is also used in same camping stoves
- (3) Crude petroleum is lighter than water.
- (4) Coal is used for the manufacturing of synthetic petrol
- (5) Ethylene is the hormone that causes tomatoes and apples to ripen
- (6) Oxyacetylene torch is used for cutting of metals
- (7) Methane is used to manufacture urea fertilizer
- (8) Kekule was the scientist who draw the structure of benzene

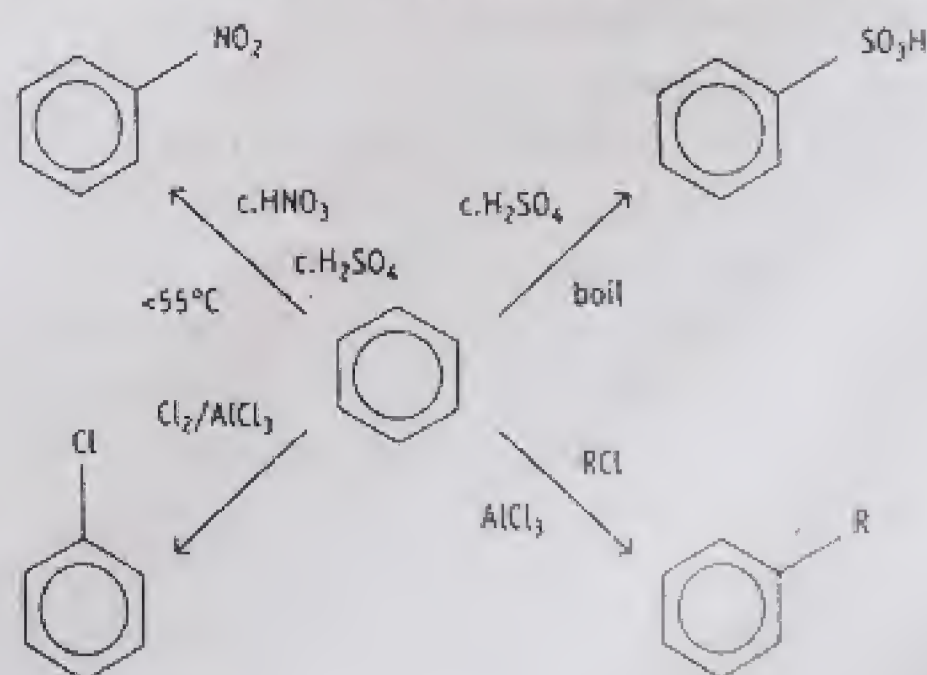


## KEY POINTS

- Compared to other functional groups, alkanes tend to have low melting and boiling points and very low solubility in polar solvents such as water.
- Alkanes are the simplest organic compounds, comprised of only  $sp^3$  hybridized C and H atoms connected by  $\sigma$  bonds. They have a generic formula of  $C_nH_{2n+2}$ .
- Branched alkanes are more stable than linear alkanes, e.g. 2-methylpropane is more stable than n-butane.
- Alkanes react with halogens by a radical mechanism to give haloalkanes. The mechanism consists of three steps, initiation, propagation and termination.
- Alkenes are unsaturated hydrocarbons with at least one  $C=C$ . the double bond is composed of a  $\sigma$  and a  $\pi$  bond. Carbon atoms in alkenes are  $sp^2$  hybridized.
- Alkenes are very reactive compounds. They undergo electrophilic reactions very easily.
- Addition of unsymmetrical reagent to an unsymmetrical alkene takes place in accordance with the Markownikov's Rule.
- Compounds that have the same molecular formula but different chemical structures are called isomers.

**Constitutional** (or structural) isomers differ in the order in which the atoms are connected so they contain different functional groups and / or bonding patterns:

- Example:** 1-propanol, 2-propanol and ethyl methyl ether ( $C_3H_8O$ )
- Stereoisomers** contain the same functional groups and differ only in the arrangement of atoms in space.
- Conformational** isomers (or conformers or rotamers) are stereoisomers produced by rotation about sigma bonds, typically rapidly interconnecting at room temperature:
- Configurational** isomers are stereoisomers that do not readily interconvert at room temperature and can (in principle at least) be separated.
- Geometric** isomers are configurational isomers that differ in the spatial position around a bond with restricted rotation (e.g. a double bond).
- Optical** isomers are configurational isomers that differ in the 3D relationship of the substituents about one or more atoms.
- Enantiomers** are optical isomers that are non-superimposable mirror images.
- Diastereomers** are optical isomers that are not enantiomers.
- Hydrocarbons containing a triple bond are known as alkynes or acetylenes.
- Alkynes undergo addition reactions and two molecules of a reagent are added in it.
- The decreasing reactivity order of alkanes, alkenes and alkynes are as follows: Alkenes > Alkynes > Alkanes
- Aromatic hydrocarbons include benzene and all those compounds that are structurally related to benzene.
- Aromatic hydrocarbons containing one benzene ring in their molecules are called monocyclic aromatic hydrocarbons.
- Aromatic hydrocarbons containing two or more benzene rings in their molecules are called polycyclic aromatic hydrocarbons.
- The electrons in benzene are loosely held and the ring acts as a source of electrons. Hence benzene is readily attacked by electrophiles in the presence of a catalyst.
- Since electrophilic substitutions reaction lead to resonance stabilized benzene derivatives so substitution are the main reaction of benzene.
- Resonance energy of benzene is 152kJ/mole.
- Structure of benzene is the resonance hybrid of two Kekule's structures and three Dewar's structures.
- The  $C_6H_5-$  group is called phenyl
- The characteristic reaction type of benzene is electrophilic substitution. Some important substitution reactions are shown on the following diagram



- Groups like  $NH_2$ ,  $NHR$ ,  $-OR$ ,  $-SH$ ,  $-OCOR$ ,  $-X$ ,  $-OH$  etc which increase the electron density in the nucleus and facilitate further electrophilic substitutions are known as ortho- and para- directing groups.
- Groups like  $CN$ ,  $-CHO$ ,  $NH_3$ ,  $NR_3$ ,  $CCl_3$  which hinder further substitution in the benzene nucleus are known as meta-directing groups.



## EXERCISE

**Q1: Select the right answer from the choices given with each question.**

- (i) The molecule of ethane posses which hybridization;  
 (a)  $sp^3$  (b)  $sp^2$  (c)  $sp$  (d)  $sp^2d$
- (ii) The  $sp^2$  hybrid orbitals are oriented in space at one angle;  
 (a)  $109.5^\circ$  (b)  $180^\circ$  (c)  $100^\circ$  (d)  $120^\circ$
- (iii) The geometry of acetylene is,  $sp$   
 (a) angular (b) bent (c) trigonal (d) linear
- (iv) Which reaction is used as test for the presence of alkene; Baeyer's test  
 (a) reaction of cold diluted alkaline  $KMnO_4$  (b) Combustion  
 (c) Polymerization (d) Catalytic hydrogenation
- (v) The general formula of alkane is;  
 (a)  $C_nH_{2n+2}$  (b)  $C_nH_n$  (c)  $C_nH_{2n}$  (d)  $C_nH_{2n-2}$
- (vi) Soda lime is;  
 (a) NaOH (b) KOH (c) Mixture of Na and Ca hydroxide (d) CaO and NaOH
- (vii) The marsh gas is  
 (a) Ethane (b) Methane (c) Propane (d) Butane
- (viii) Acidic hydrogen is present in  $H-C \equiv C-H$   
 (a) Acetylene (b) Ethane (c) Benzene (d) Ethene
- (ix) The benzene molecule contains:  
 (a) Three double bonds (b) Two double bonds (c) One double bond (d) None of these
- (x) The electrophile in aromatic sulphonation is;  
 (a)  $H_2SO_4$  (b)  $HSO_4^-$  (c)  $SO_3$  (d)  $SO_4^{2-}$
- (xi) The conversion of n-hexane into benzene by heating in the presence of Pt is called;  
 (a) Isomerization (b) Aromatization (c) Dealkylation (d) Rearrangement
- (xii) Catalyst used for Friedel Craft's reaction is;  
 (a)  $HNO_3$  (b)  $AlCl_3$  (c)  $BeCl_3$  (d) NaCl
- (xiii) Benzene cannot undergo  
 (a) Elimination (b) Substitution (c) Oxidation (d) Addition
- (xiv) Shape of benzene molecule is  
 (a) Pyramidal (b) Linear planar (c) Trigonal (d) Hexagonal planar
- (xv) In which one of the following compounds the benzene ring are isolated;  
 (a) Naphthalene (b) Anthracene (c) Phenanthrene (d) Diphenyl methane
- (xvi) Two compounds have the same composition and also have the same atoms attached to the same atoms although with different orientations in space. These compounds are  
 (a) identical (b) Position isomers (c) structural isomers (d) stereoisomers
- (xvii) The isomers of a substance must have  
 (a) same chemical properties (b) same molecular weight  
 (c) same structural formula (d) same functional groups
- (xviii) Ethanol and dimethyl ether are best considered:  
 (a) structural isomers (b) stereoisomers (c) enantiomers (d) diastereomers
- (xix) Alkenes show geometrical isomers due to  
 (a) asymmetry (b) rotation around a single bond  
 (c) resonance (d) restricted rotation around a double bond
- (xx) Geometrical isomerism is shown by  
 (a) lactic acid (b) maleic acid (c) 1-butene (d) 1,1-dichloroethylene



(xxi) A molecule is said to be chiral

(a) if it contains plane of symmetry

(c) if it cannot be superimposed on its mirror image

(b) if it contains center of symmetry

(d) if it can be superimposed on its mirror image

(xxii) Which of the statements is false regarding chiral compounds

(a) rotate the plane of polarized light

(c) exist as enantiomers

(b) have cis and trans isomers

(d) can be detected with a polarimeter

(xxiii) An optically active compound

(a) must contain at least four carbons

(b) when in solution rotate the plane of polarized light

(c) must always contain an asymmetric carbon atom

(d) in solution always give a negative reading in polarimeter

(xxiv) Plane polarized light is affected by

(a) identical molecules

(b) all polymers

(c) chiral molecules

(d) all biomolecules

(xxv) It is possible to distinguish between optical isomers

(a) by using chemical tests

(b) by mass spectrometry

(c) by IR spectroscopy

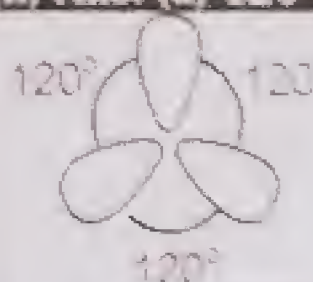
(d) by polarimetry

## ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (a)  $sp^3$

In ethane, both carbon atoms are  $sp^3$ -hybridized because each of them is attached with four atoms.

(ii) Ans: (d)  $120^\circ$



$sp^2$  hybridized orbitals

(iii) Ans: (d) linear

Both carbon atoms of acetylene are  $sp$ -hybridized. So, the molecule of acetylene is linear with  $180^\circ$  angles.  
 $H-C \equiv C-H$

(iv) Ans: (a) reaction of cold diluted alkaline  $KMnO_4$

The colour of  $KMnO_4$  is discharged by an alkene. This test is called Baeyer's test.

(v) Ans: (a)  $C_nH_{2n+2}$

The alkanes are saturated compounds, so their general formula is  $C_nH_{2n+2}$ . e.g., the formula of ethane is  $C_2H_6$ .

(vi) Ans: (d)  $CaO$  and  $NaOH$

Soda is  $NaOH$  and lime is  $CaO$ .

(vii) Ans: (b) Methane

Methane is found in marshy places (گدازلی علاقے), so it is called marsh gas.

(viii) Ans: (a) Acetylene

The hydrogen atom attached to an  $sp$ -hybridized carbon atom shows acidic nature. Thus, acetylene molecule contains acidic hydrogen.  $H-C \equiv C-H$ . All terminal alkynes also contain acidic hydrogen.

(ix) Ans: (d) None of these

In benzene molecule, the six  $p$ -orbitals of six carbon atoms overlap with each other to form a continuous delocalized  $p$ -electron cloud sheath. So, actually, three double bonds are not present.

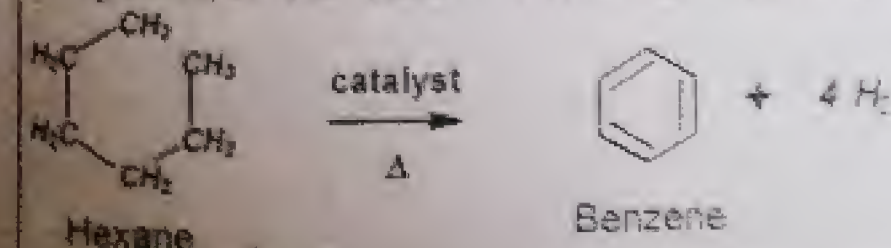
(x) Ans: (c)  $SO_2$

During sulfonation,  $SO_3$  electrophile is generated as



(xi) Ans: (b) Aromatization

Since an aromatic compound is prepared from an aliphatic compound, so this reaction is called aromatization.



(xii) Ans: (b)  $AlCl_3$

$AlCl_3$  is a Lewis acid and therefore it is used as a powerful electrophile in Friedel-Craft's reactions e.g.



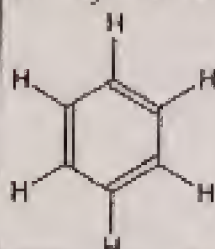


**(xiii) Ans: (a) Elimination**

Benzene give substitution, oxidation and addition reactions only. Elimination reactions are not possible.

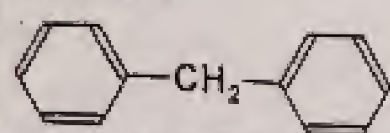
**(xiv) Ans: (d) Hexagonal planar**

X-rays analysis has shown benzene to be hexagonal planar.



**(xv) Ans: (d) Diphenyl methane**

In Diphenyl methane, both benzene rings are isolated from each other.



**(xvi) Ans: (d) stereoisomers**

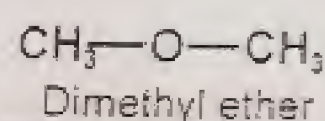
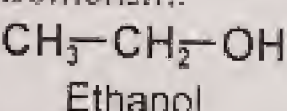
By definition, the compounds having same composition, same atoms attached to the same atoms but with different orientations in space are stereoisomers and the phenomenon called stereoisomerism.

**(xvii) Ans: (b) same molecular weight**

The isomers have same molecular formula. Hence, they must have same molecular weight as well.

**(xviii) Ans: (a) structural isomers**

Ethanol and dimethyl ether have same molecular formula ( $C_2H_6O$ ) but different functional groups. So they are functional group isomers of each other which is a type of structural isomerism.

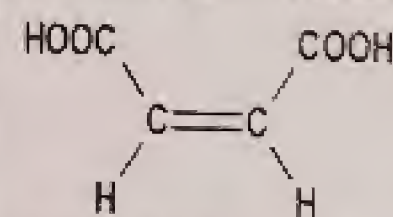


**(xix) Ans: (d) restricted rotation around a double bond**

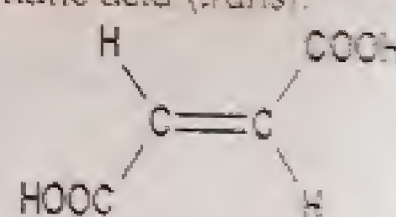
Free rotation cannot occur around double bond. So, the rotation is restricted and geometrical isomerism is resulted.

**(xx) Ans: (b) maleic acid**

Maleic acid fulfils the conditions of geometrical isomerism and is a cis-isomer. Its other isomer is fumaric acid (trans).



Maleic acid (cis-isomer)



Fumaric acid (trans-isomer)

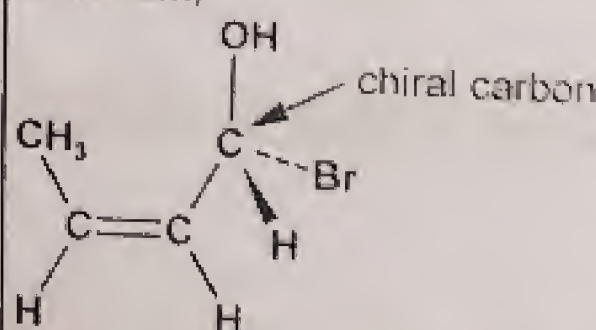
**(xxi) Ans: (c) if it cannot be superimposed on its mirror image**

By definition, a molecule which has non-superimposable mirror image is called a chiral molecule and it will show optical activity.

**(xxii) Ans: (b) have cis and trans isomers**

cis- and trans-isomerism is geometrical isomerism. It is related to the chiral nature of molecule.

(NOTE: A chiral molecule may also show geometrical isomerism if it fulfils the conditions of geometrical isomerism as well e.g. the following compound will show both geometrical and optical isomerism)



**(xxiii) Ans: (b) when in solution rotate the plane of polarized light**

An optically active compound must rotate the plane of polarized light.

**(xxiv) Ans: (c) chiral molecules**

Chiral molecules are optically active molecules. Thus, they rotate the plane of polarized light.

**(xxv) Ans: (d) by polarimetry**

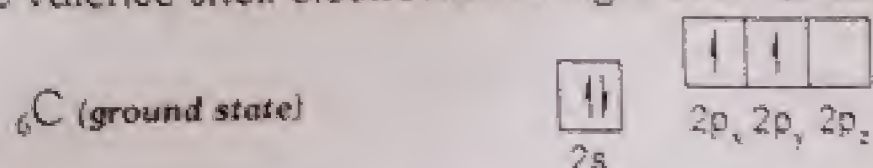
Optically isomers can rotate the plane of polarized light in different directions. Thus they can be identified by polarimetry.



**Q2: Give brief answers for the following questions.**

**1. Why carbon is  $sp^3$  hybridized in the compounds?**

The valence shell electronic configuration of carbon is



So, only two p-orbitals of C are partially filled, therefore Carbon must form two bonds. However, carbon is tetravalent in most of its compounds. Thus, in excited state of carbon, an electron from 2s orbital is promoted to an empty  $2p_z$  orbital. i.e.,



Thus C-atom becomes tetravalent. However, since there is one s-orbital and three p-orbitals for bond formation, therefore, valency is not equivalent. So, the four orbitals of C are mixed together to give four  $sp^3$ -hybrid orbitals which are used to form bonds with other elements in a tetrahedral geometry.

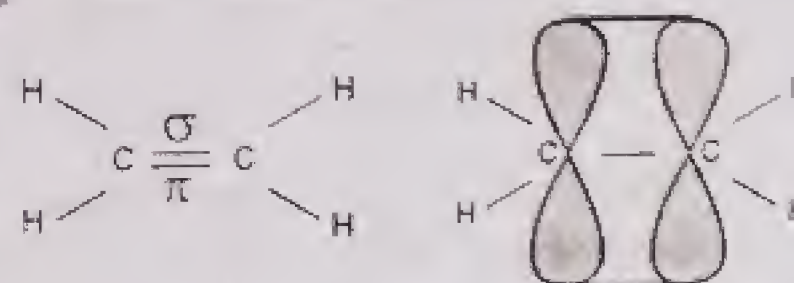
Hence, to explain the equivalent tetravalency and tetrahedral geometry of carbon atoms in compounds, the idea of  $sp^3$ -hybridization is used.

**2. How is pi-bond formed in alkenes and alkynes?**

**PI-bond formation in Alkenes**

Consider the example of Ethene ( $\text{C}_2\text{H}_4$ )

- In  $\text{C}_2\text{H}_4$ , both carbon atoms show  $sp^2$ -hybridization.
- The three  $sp^2$ -hybridized orbitals of each carbon atom are used to form C-C and C-H  $\sigma$ -bonds.
- One unhybridized  $2p_z$ -orbital of two carbon atoms overlap sideways to form a  $\pi$ -bond.

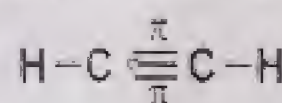
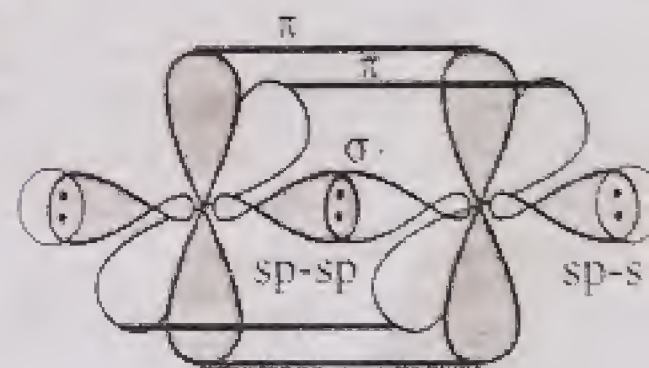


$\pi$ -bond formation

**PI-bond formation in Alkynes**

Consider the example of Ethyne ( $\text{C}_2\text{H}_2$ )

- In  $\text{C}_2\text{H}_2$ , both carbon atoms show  $sp$ -hybridization.
- The two  $sp$ -hybridized orbitals of each carbon atom are used to form C-C and C-H  $\sigma$ -bonds.
- The unhybridized  $2p_y$  and  $2p_z$  orbitals of two carbon atoms overlap sideways to form two  $\pi$ -bonds.



In  $\pi$ -bonds probability of finding electron is present above and below the internuclear axis.

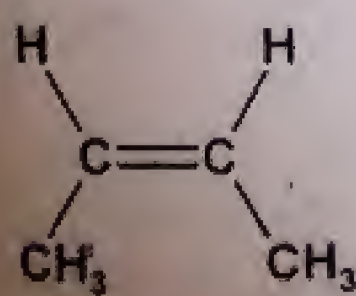
**3. What is cis-trans isomerism?**

Geometrical isomerism (also called cis-trans isomerism) results from a restriction in rotation about double bonds or about single bonds in cyclic compounds.

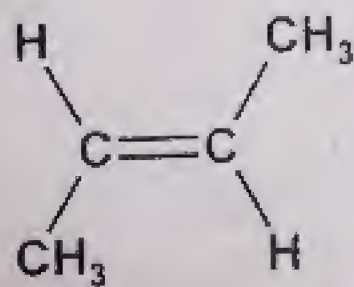
**Conditions for cis-trans isomerism**

- Presence of double bond or cyclic ring
- Two different groups must be attached, to each carbon of double bond, or to different carbons of cyclic ring

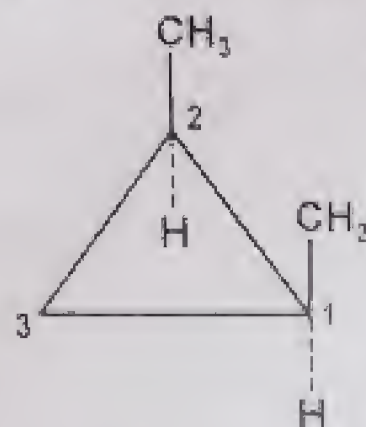
**Examples:**



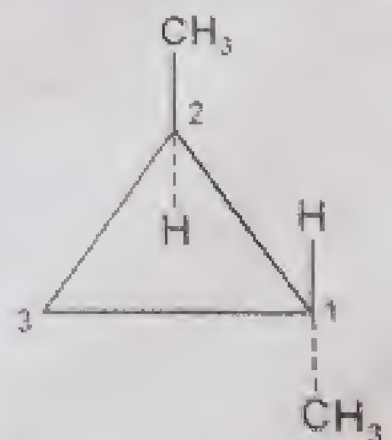
cis-2-Butene



trans-2-Butene



cis-1,2-Dimethylcyclopropane



trans-1,2-Dimethylcyclopropane



**4. Why alkanes are relatively chemically inert?**

Alkanes are highly unreactive. Hence these are also called Paraffin. (Latin, Parum = little, affins = affinity)  
Unreactivity of Alkanes is due to two factors

**(i) Inertness of  $\sigma$ -bond**

In a  $\sigma$ -bond the electrons are very tightly held between the nuclei. A lot of energy is required to break. Moreover, the electrons present in a  $\sigma$ -bond cannot attack on any electrophile. Also no nucleophilic attack on them. Hence Alkanes less reactive.

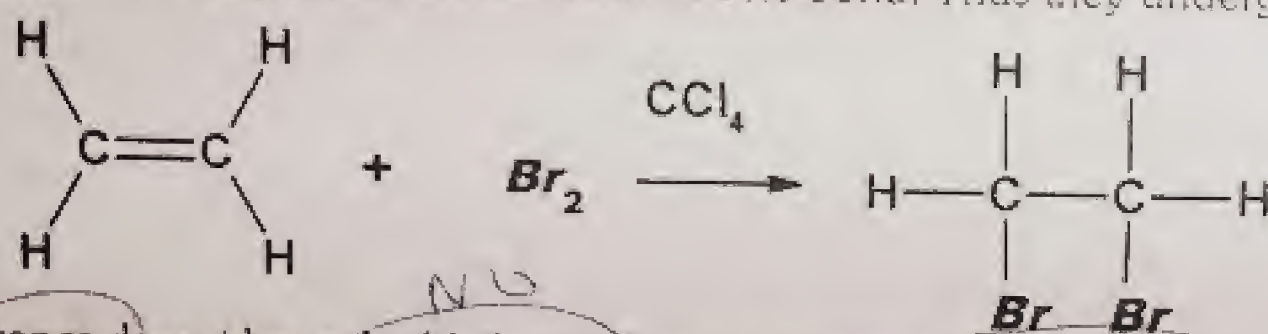
**(ii) Non-polar Bonds:**

The electronegativity of carbon (2.5) and hydrogen (2.1) do not differ appreciably. Therefore, the electrons between C-H and C-C are equally shared and bonds become non-polar. Hence, the ionic reagents such as acids, alkalis, oxidizing agents, etc. find no place in the alkane molecules for reaction.

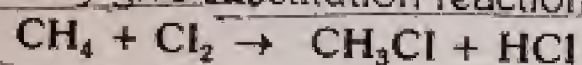
Hence, alkanes are chemically inert

**5. Alkenes usually undergo addition reactions while alkanes do not why?**

Alkenes are unsaturated and contain double bond. Thus they undergo electrophilic addition reaction. e.g.



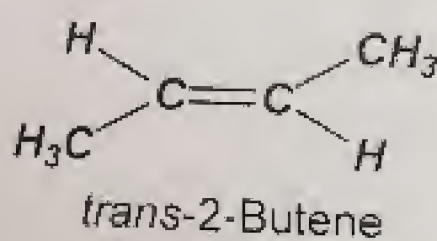
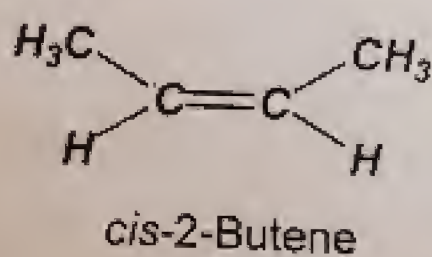
Alkanes do not have double bond. They are saturated compounds so they do not give addition reaction. Instead they give substitution reactions. e.g.

**6. What is stereoisomerism?**

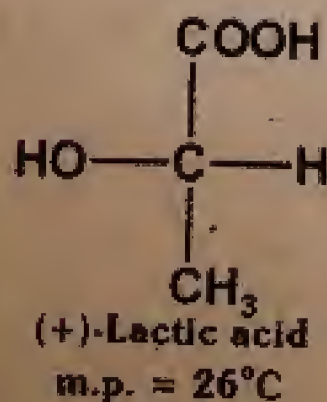
The isomers having equal number of same types of bonds with identical connectivity, but different arrangement of atoms in space are called stereoisomers and the phenomenon is called stereoisomerism. Study of such isomers is called stereochemistry.

It is of two types

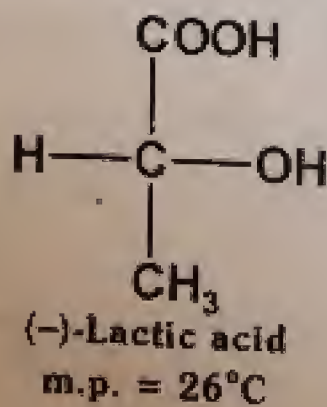
(a) Geometrical Isomerism or *cis*, *trans*-isomerism: Example



(b) Optical Isomerism



Mirror



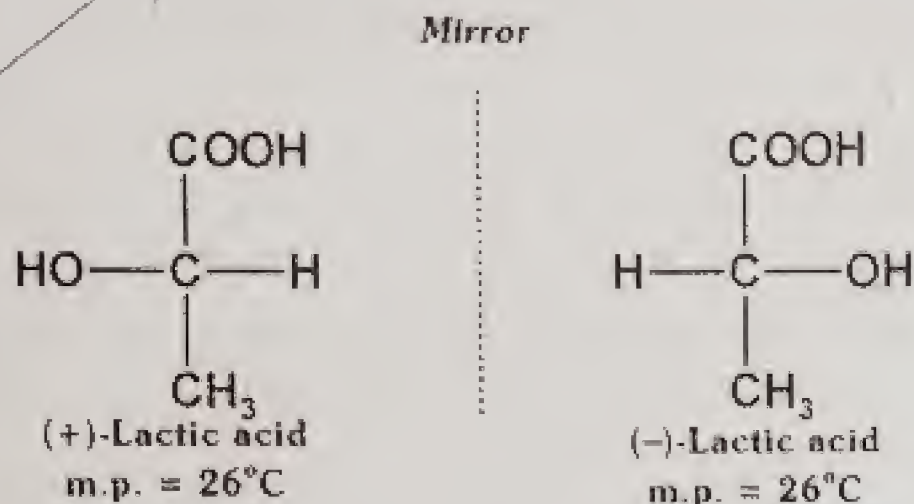
C<sub>3</sub> (H<sub>2</sub>O)<sub>3</sub>



### 7. How optical isomers arise?

- An asymmetric molecule has non-superimposable mirror image. Such a molecule shows optical activity. It is also called a chiral molecule.
- The optically active compound can exist in two isomeric forms which rotate the plane polarized light in opposite directions. These are called Optical Isomers and the phenomenon is known as Optical Isomerism.
- The optical isomers have same atoms and same connectivity of atoms. However, they differ in spatial (3-D) arrangement of atoms.

Example:

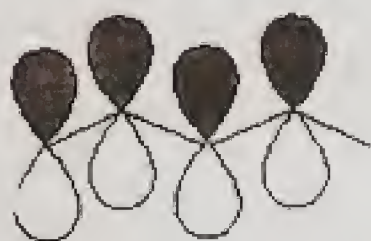
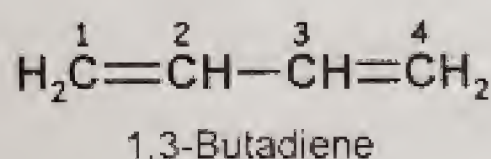


### 8. What are conjugated bonds formed?

The word "**conjugation**" is derived from a Latin word that means "to link together".

In organic chemistry, it is used to describe the situation that occurs when p-systems are "linked together". Thus, an "**extended**" p-system exists over a longer series of atoms (e.g.  $\text{C}=\text{C}-\text{C}=\text{C}$  or  $\text{C}=\text{C}-\text{C}=\text{O}$  etc.).

Example:



### 9. Why alkenes are more reactive than alkynes?

- Both alkenes and alkynes contain pi bonds. The electrons of pi-bond are exposed to attack by electrophiles.
- In alkynes, a triple bond is present. Due to high electrons density between carbon atoms, the  $\text{C}\equiv\text{C}$  triple bond is shorter (1.20 Å) than the  $\text{C}=\text{C}$  double bond (1.33 Å).
- Due to shorter bond length, the pi-electrons of a triple bond are less exposed and less reactive than alkenes towards electrophilic reagents.

### 10. Justify the given order of reactivity? Alkenes > Alkynes > Alkanes

- In alkanes, only sigma bond is present, which is difficult to break. Hence alkanes are least reactive.
- Both alkenes and alkynes contain pi bonds. The electrons of pi-bond are exposed to attack by electrophiles.
- In alkynes, a triple bond is present. Due to high electrons density between carbon atoms, the  $\text{C}\equiv\text{C}$  triple bond is shorter (1.20 Å) than the  $\text{C}=\text{C}$  double bond (1.33 Å). Thus pi-electrons of a triple bond are less exposed and less reactive than alkenes towards electrophilic reagents.
- Thus general order of reactivity towards electrophilic reagent is  
**Alkenes > Alkynes > Alkanes**
- However, alkynes are more reactive than alkenes towards nucleophilic reagents.







10.16. Resonance energy

13. What is resonance energy?

The resonance energy of a compound is a measure of the extra stability of the conjugated system compared to the corresponding number of isolated double bonds.

Example:

The difference between experimental value for benzene and that of hypothetical cyclohexatriene is 152 kJ/mol = 292 cal/mol = 70 kcal/mol.

This benzene is 152 kJ/mol more stable than the hypothetical system. This is the resonance energy for benzene.

**Q3. Give detailed answers for the following questions.**

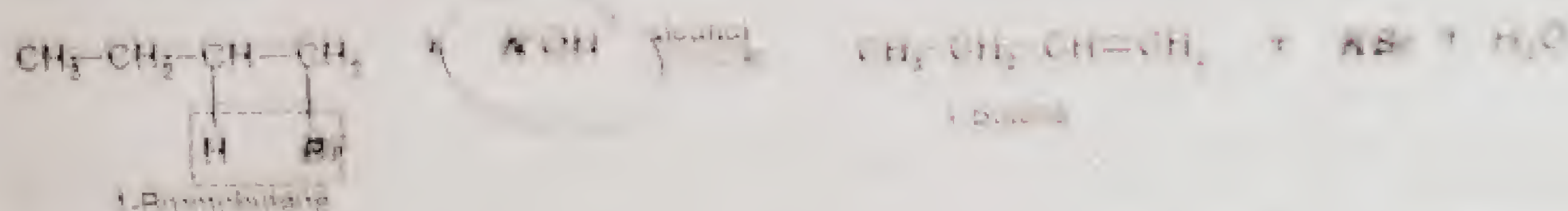
1. What is isomerism? Explain different types of isomerism?

See Page 133

2. (a) How will you prepare 1-butene from:

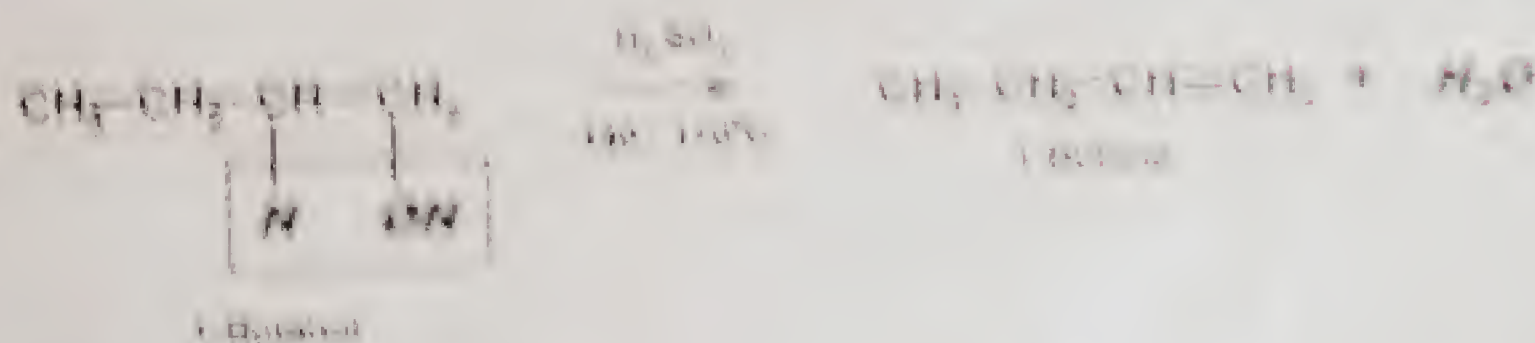
(i) an alkyl halide

When 1-bromobutane is treated with alcoholic potassium hydroxide, it undergoes elimination reaction to form 1-butene.



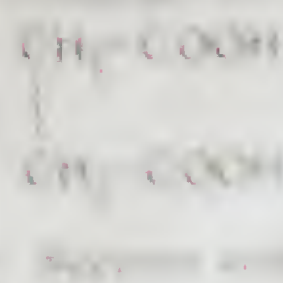
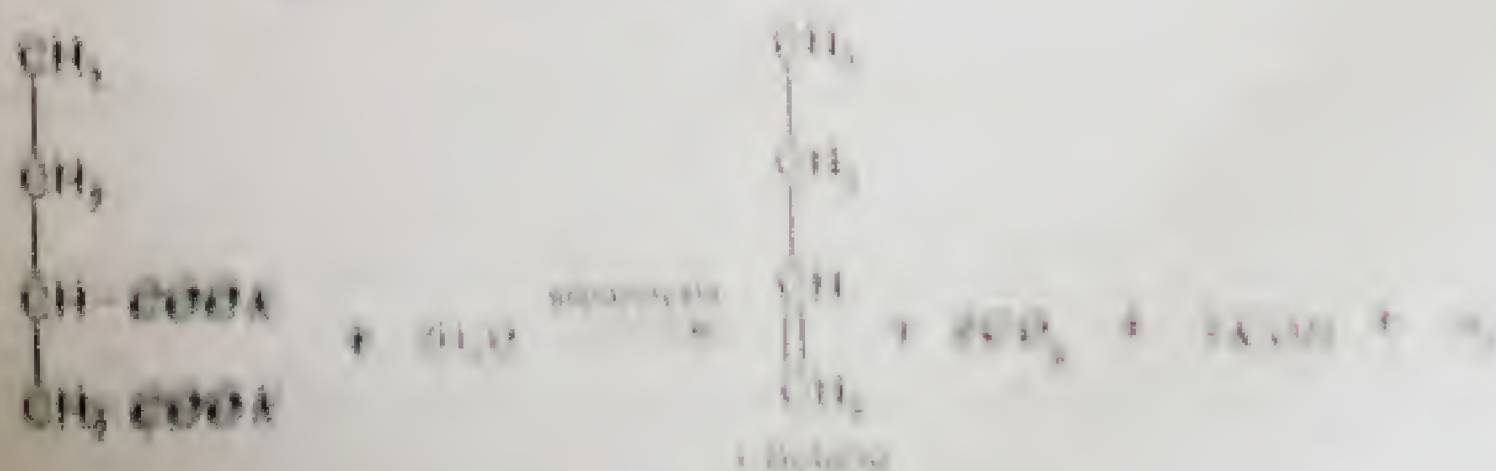
(ii) Alcohols

When vapors of 1-butanol is treated with  $\text{H}_2\text{SO}_4$  at 140-170°C, 1-butanol loses water to form 1-butene.



(iii) Electrolysis of salt

When aqueous solution of potassium salt of 1-butene is electrolyzed, it gives 1-butene. This reaction is called Kolbe's electrolysis.

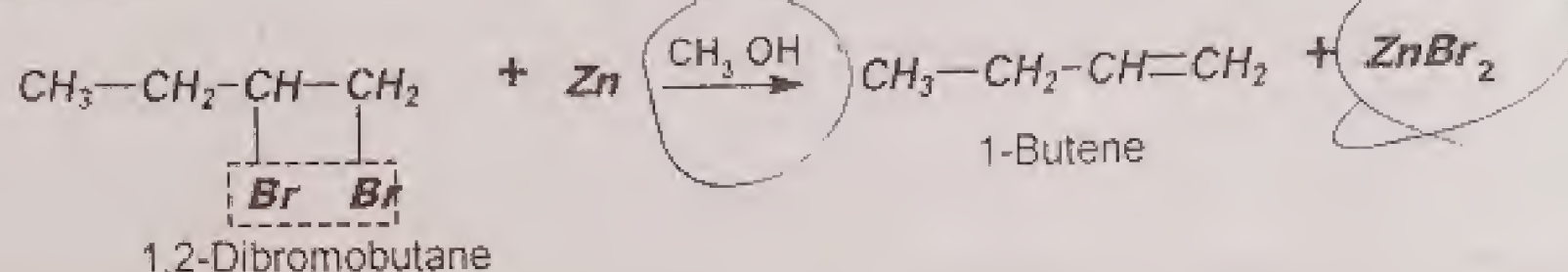




(iv) vic-Dihalides

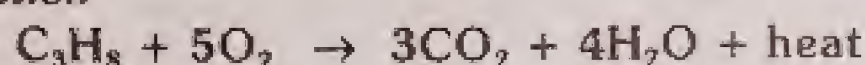
Vicinal dihalides have two halogen atoms on adjacent carbon atoms.

1,2-dibromobutane is a vicinal dihalide. When it is treated with Zn in anhydrous solvent e.g. methanol or acetic acid, it gives 1-butene.



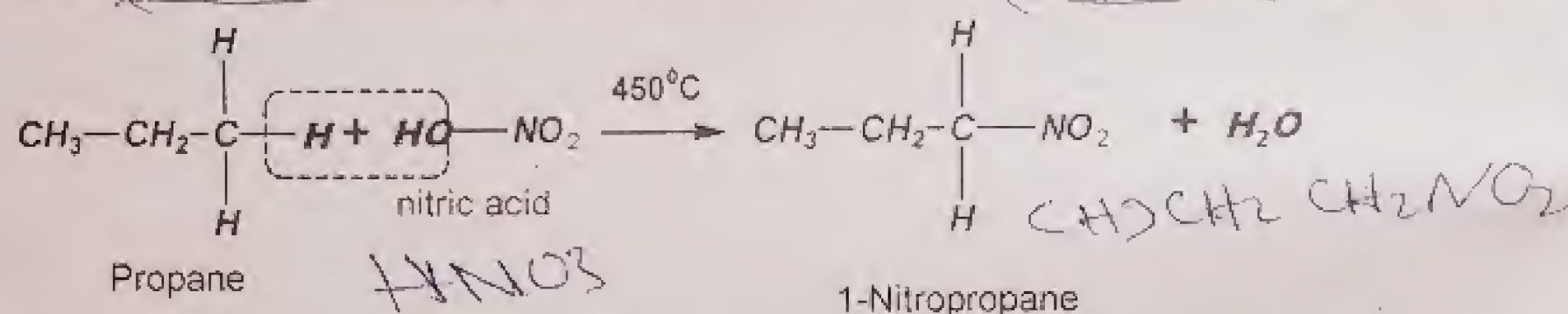
(b) What products are formed when n-propane undergo following reactions?

(i) Combustion

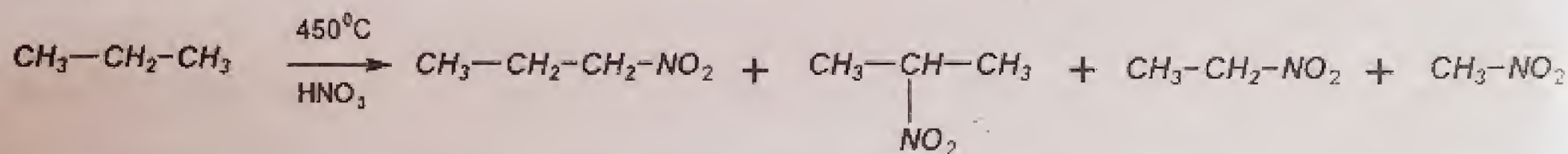


(ii) Nitration

n-Propane reacts with nitric acid in vapour-phase under drastic conditions (at 400-500°C) to give nitropropane

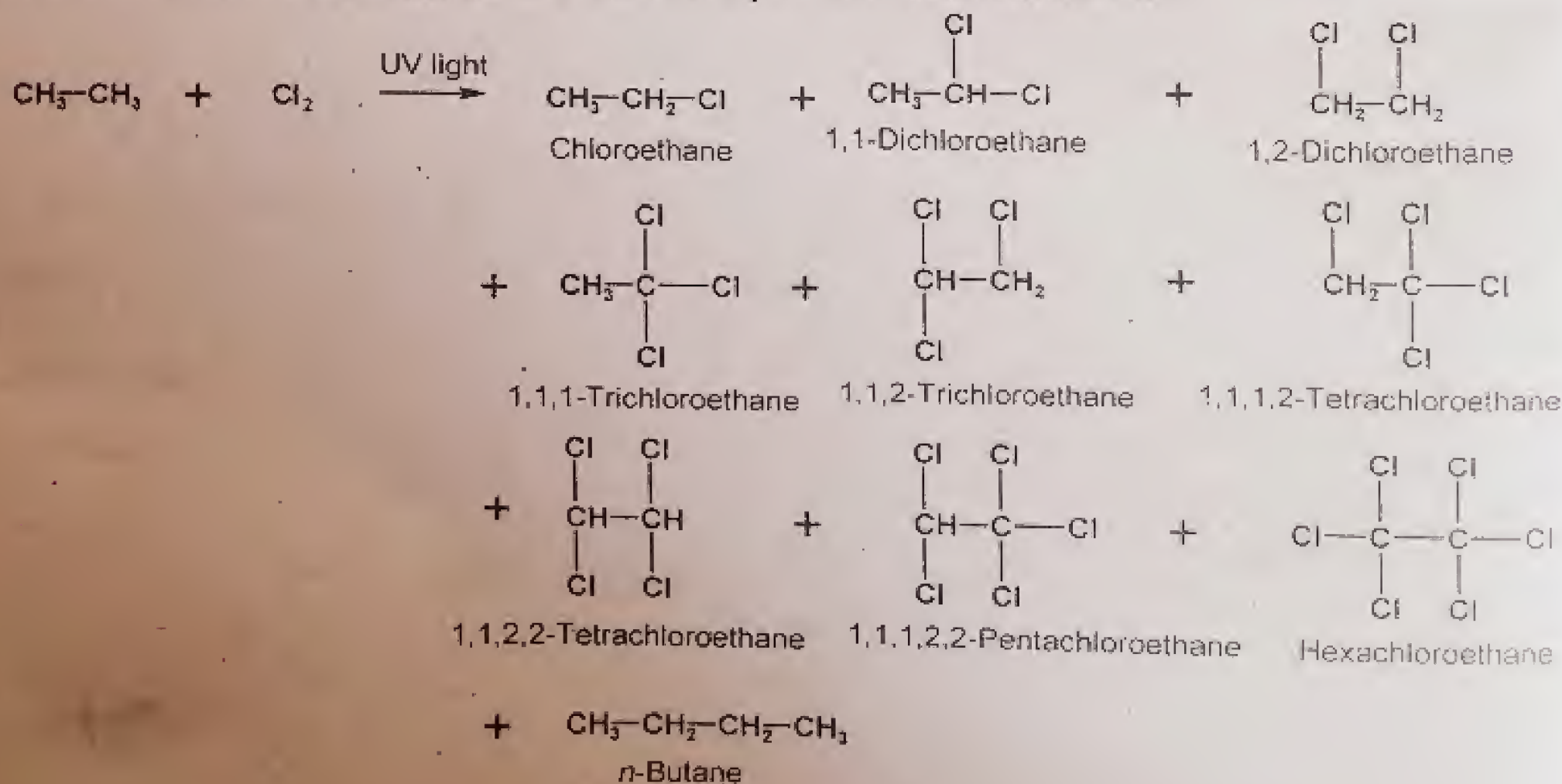


However, under drastic conditions, the molecule of n-propane is broken down and form all possible nitroalkanes.



3. (a) When ethane reacts with Cl<sub>2</sub> in UV light the mixture of products is formed. Give the detail of reaction with mechanism and all types of products.

Ethane reacts with Cl<sub>2</sub> in UV light to give a mixture of products. The reaction occurs by free radical mechanism. This reaction is called radical substitution reaction. The products of the reactions are:





### Initiation step

$$\text{Cl}-\text{Cl} \xrightarrow[\text{UV}]{h\nu} \text{Cl}^\bullet + \text{Cl}^\bullet$$
$$\text{CH}_3-\text{CH}_2-\text{H} + \text{Cl}^\bullet \longrightarrow \text{CH}_3-\dot{\text{C}}\text{H}_2 + \text{HCl}$$

Ethyl free radical

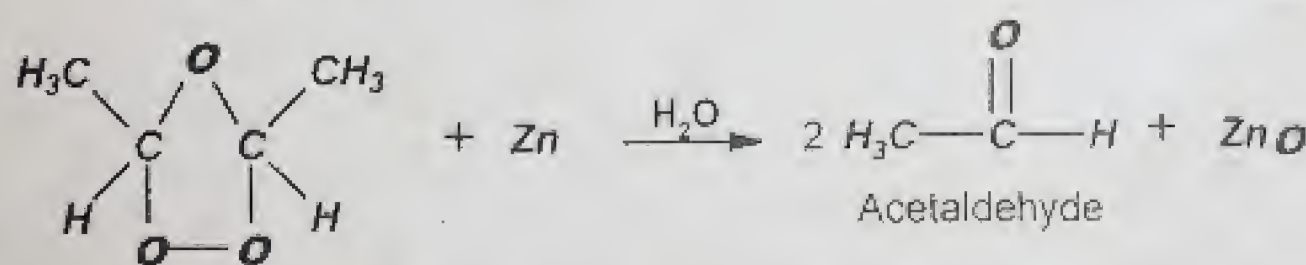
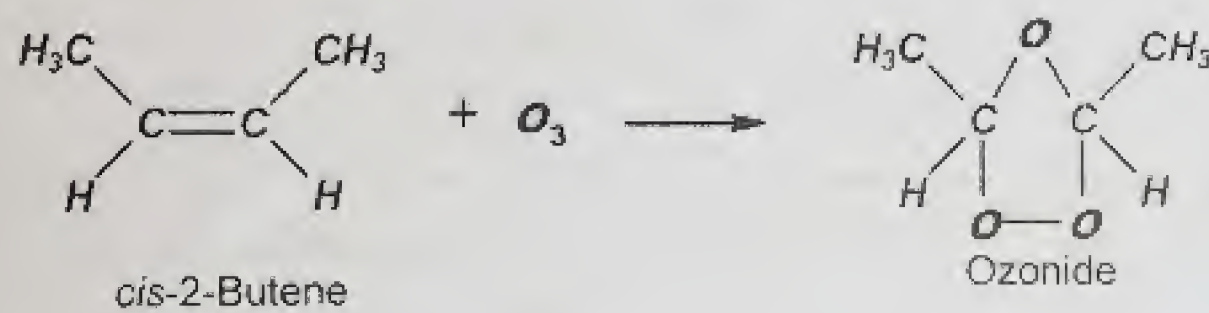


- ### Termination step


$$\text{H}_3\text{C}-\underset{\substack{| \\ \text{Br}}}{\text{CH}}-\underset{\substack{| \\ \text{Br}}}{\text{CH}}-\text{CH}_3 + \text{Zn} \xrightarrow{\text{CH}_3\text{OH}} \text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}_3 + \text{ZnBr}_2$$

2-Butene

2,3-Dibromobutane



Solved on Page 200



2. Explain the structure of benzene according to atomic orbital structure.

See on Page 194

3. Explain Friedel Craft acylation and alkylation with complete mechanism.

See on Page 196

4. Explain the following electrophilic substitution reactions of benzene with mechanism.

(a) Halogenation

See on Page 194

(b) Nitration

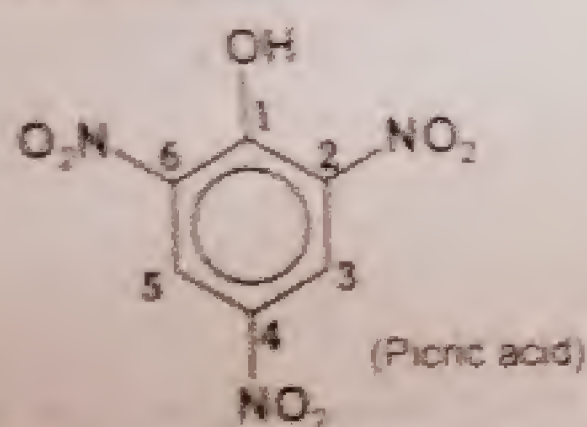
See on Page 192

(c) Sulphonation.

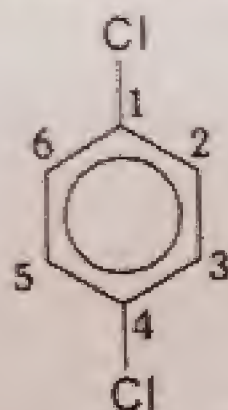
See on Page 193

7. Write the structural formulas for the following benzene derivatives:

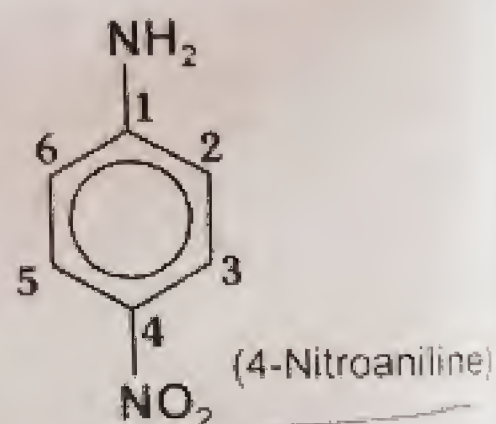
(a) 2,4,6-Trinitrophenol



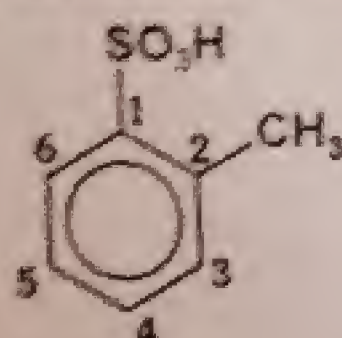
(b) 1,4-Dichlorobenzene



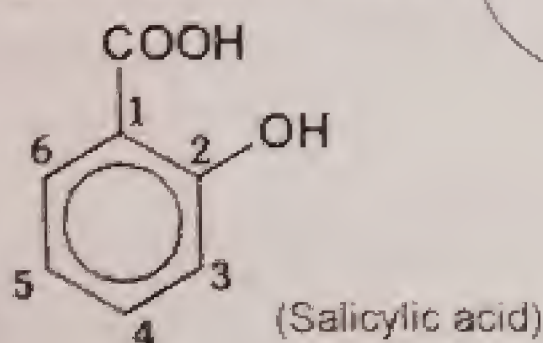
(c) 4-Nitrophenylamine



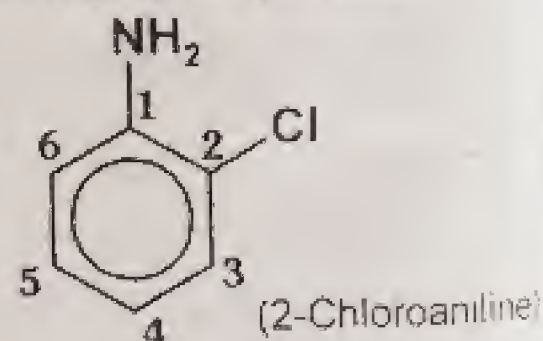
(d) 2-Methylbenzenesulphonic acid



(e) 2-Hydroxybenzoic acid

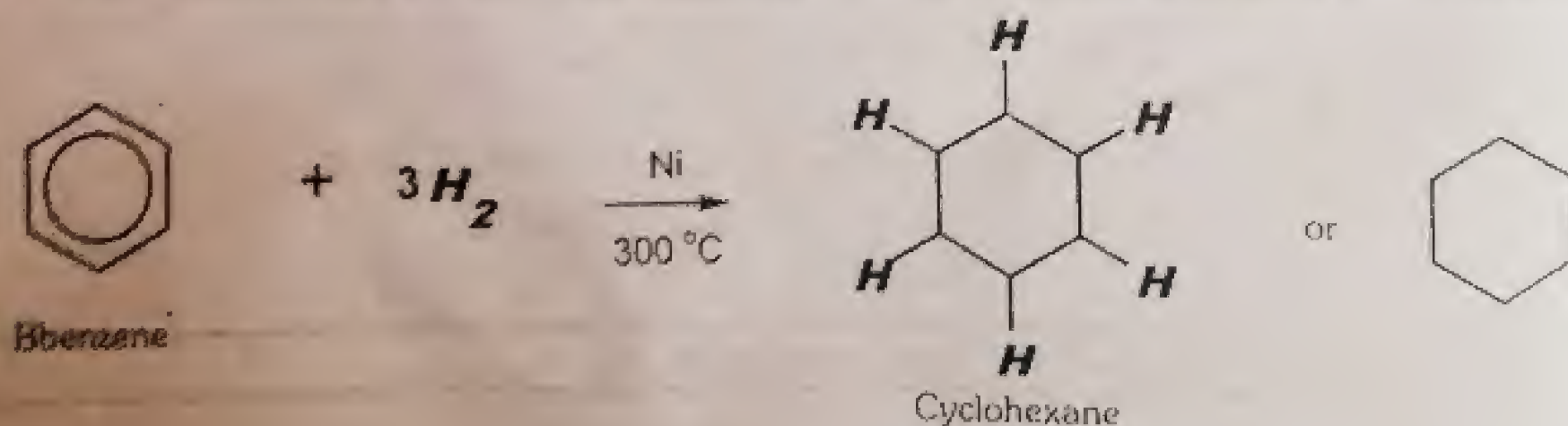


(f) 2-Chlorophenylamine



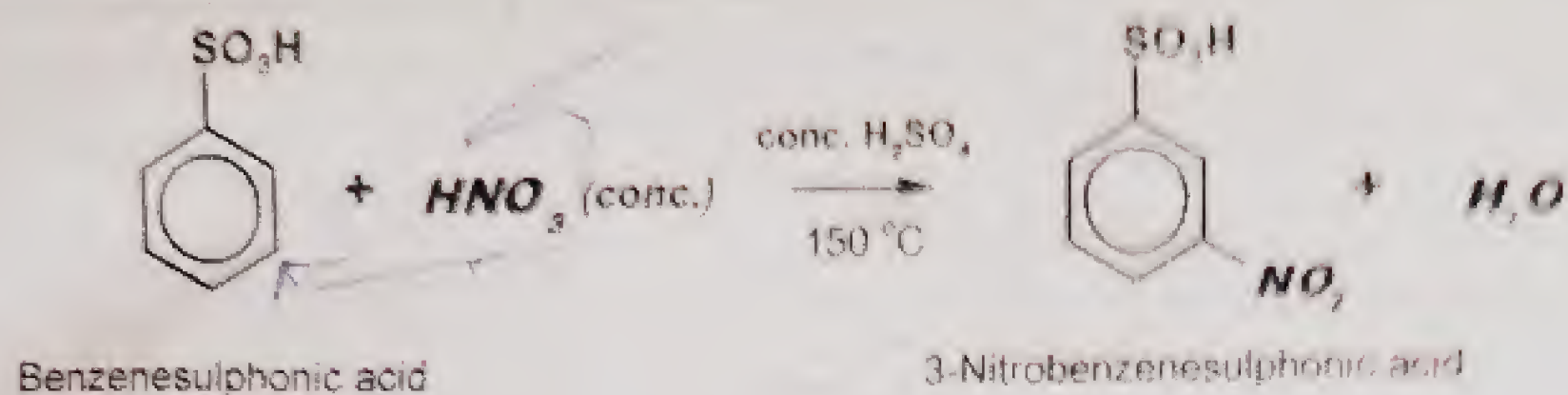
8. Predict the major products of the following reactions.

(a)

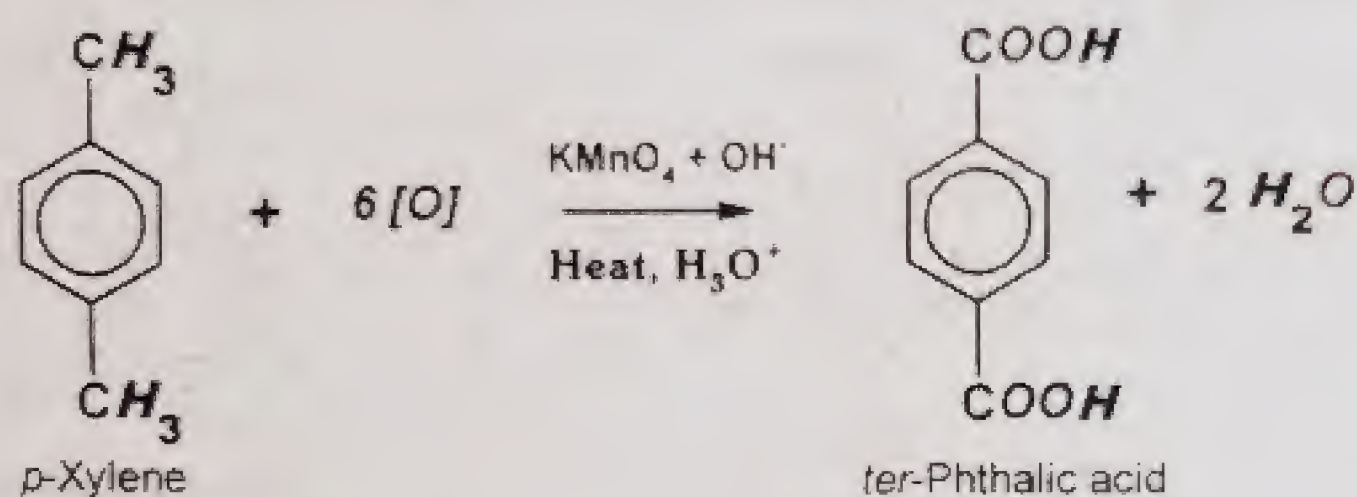




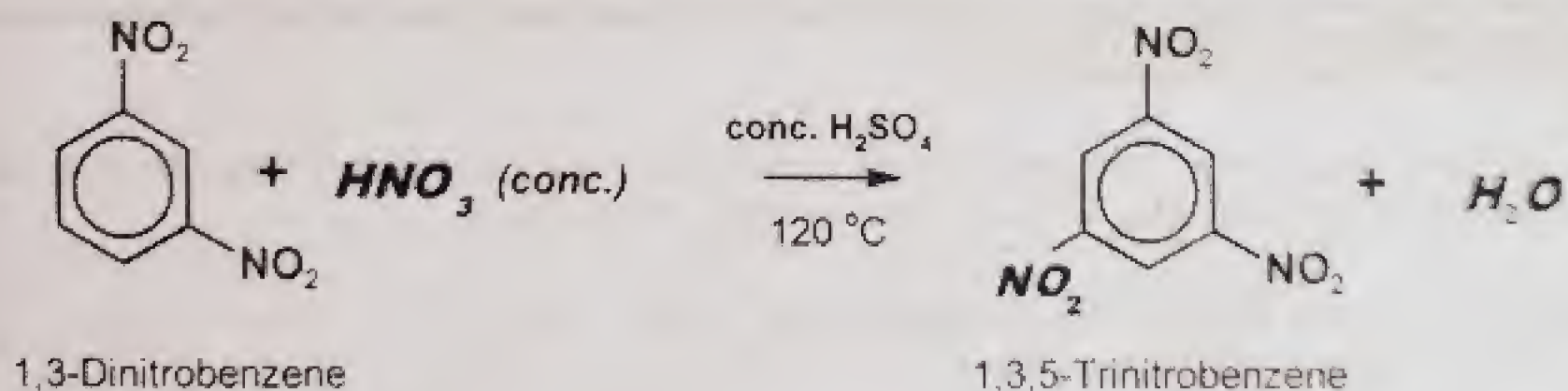
(b)



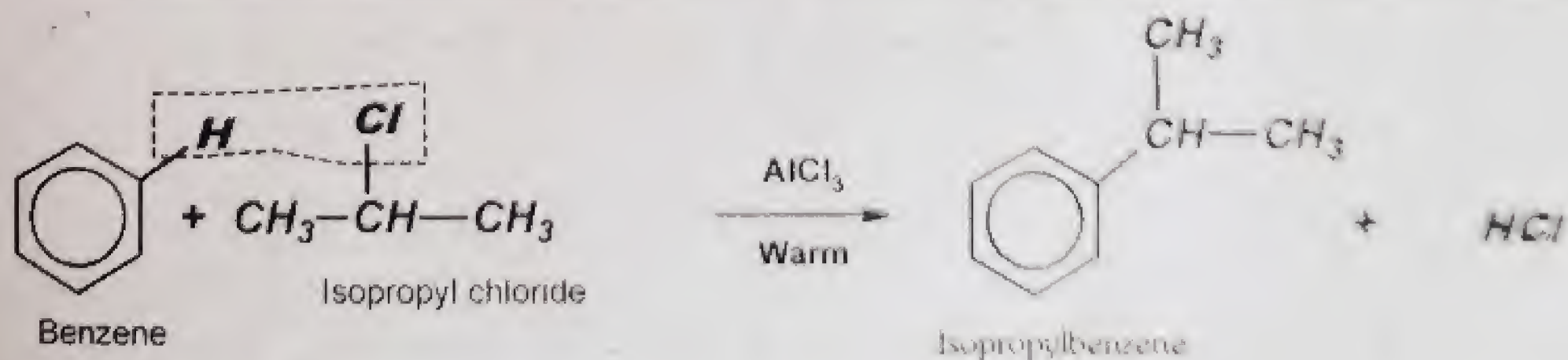
(c)



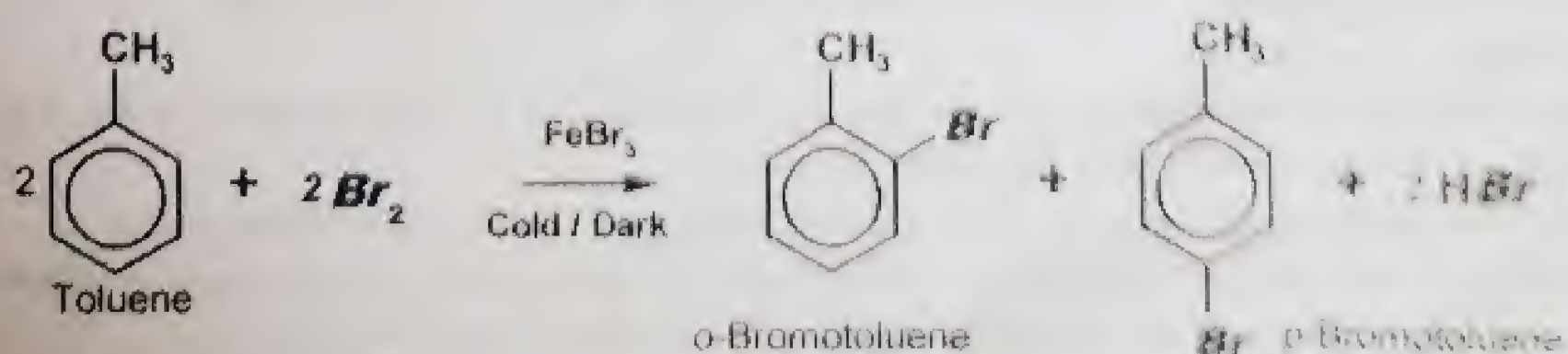
(d)



(e)

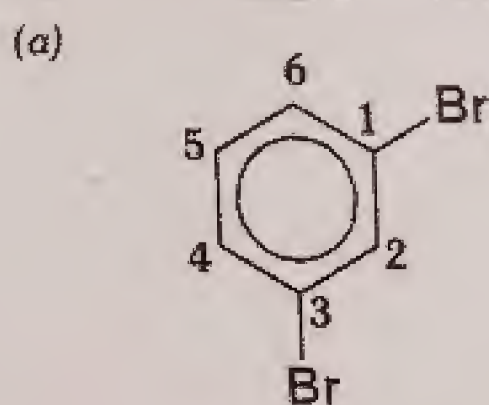


(f)

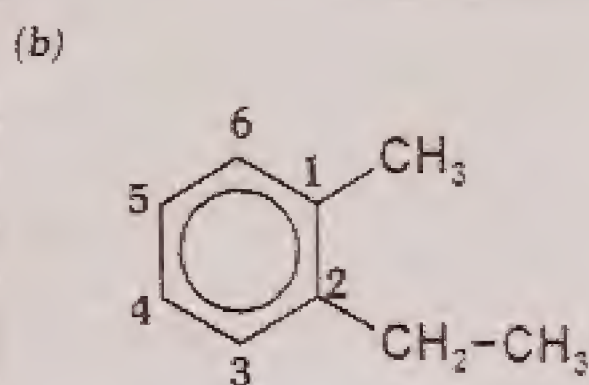




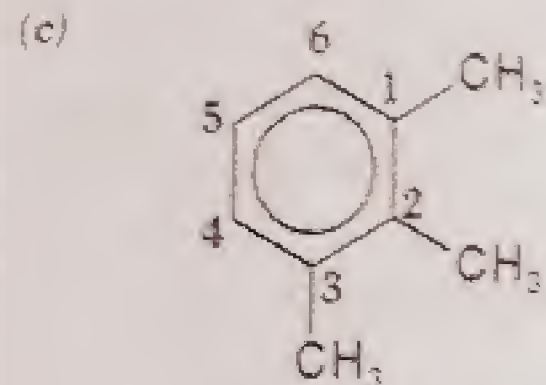
9. Name the following benzene derivatives:



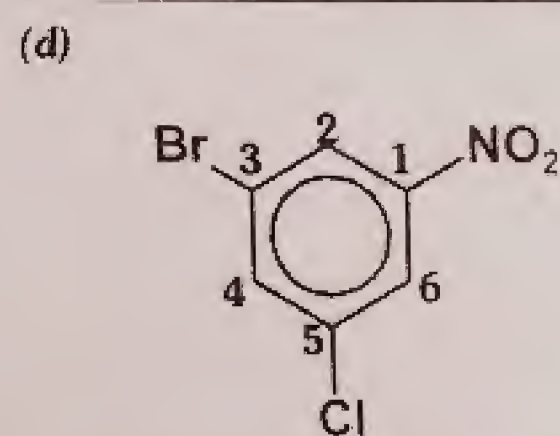
1,3-Dibromobenzene



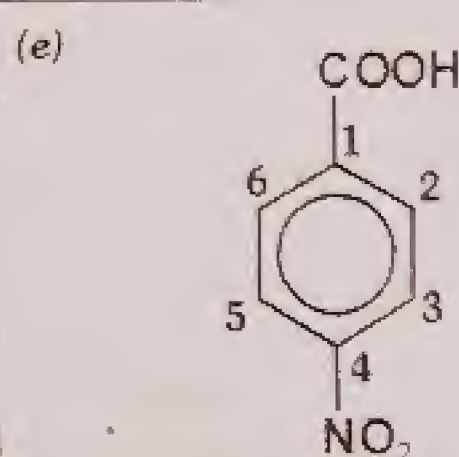
2-Ethyltoluene



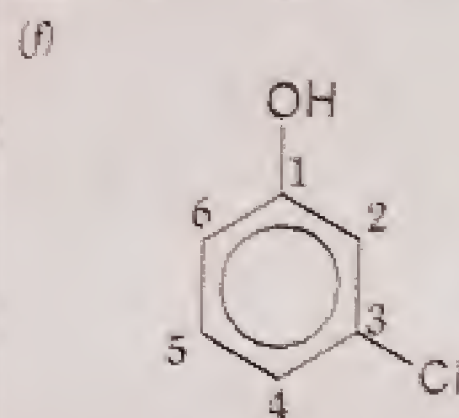
1,2,3-Trimethylbenzene



3-Bromo-5-chloronitrobenzene



4-Nitrobenzoic acid



3-Chlorophenol

### Why Groups are ortho/para and meta-directors?

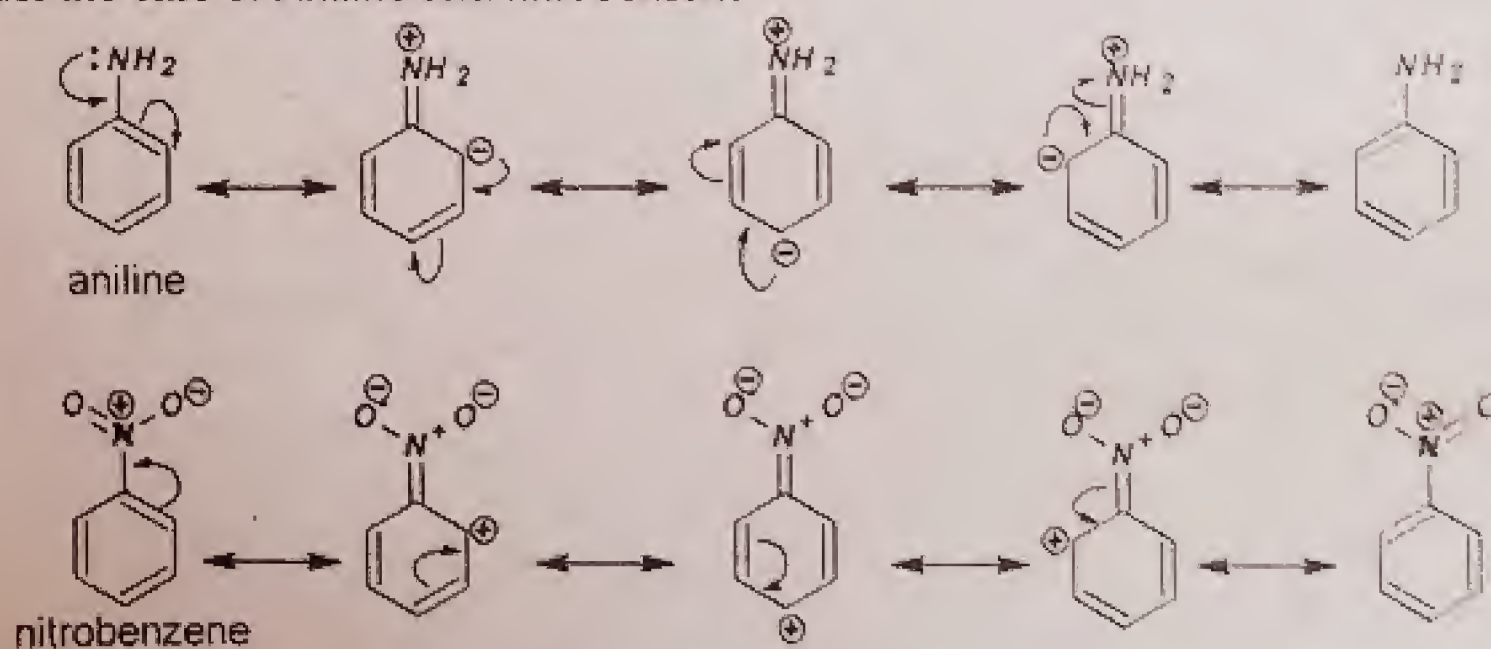
#### Resonance Effect:

The decrease in electron density at one position in a molecule, with corresponding increase in electron density at some other position is called Resonance Effect or Mesomeric Effect.

#### Examples

In delocalized chemical systems, electron density spread over various atoms.

e.g. consider the case of Aniline and nitrobenzene



Thus,  $\text{NH}_2$  donates electron to the ring while  $\text{NO}_2$  group withdraws electrons from the ring.

#### Following things should be noted.

- In case of aniline, the negative charge comes at ortho/para-positions. So, the electrophile will attack at these positions. So,  $\text{NH}_2$  group is an ortho/para director. Moreover, since the electron density is increased on the ring, so it is an activating group.
- In case of nitrobenzene, the positive charge comes at ortho/para-positions. So, the electrophile will not attack at these positions. Rather it will attack on meta-positions. So,  $\text{NO}_2$  group is a meta director. Moreover, since the electron density is decreased on the ring, so it is a deactivating group.
- Similarly others can also be explained.



**TEST YOUR SKILLS**

**IMPORTANT CONCEPTS**

05/11/18

Time: 20 Minutes

Chapter 11

Notes: (1) For writing, writing, drawing, using blue pen only. (2) Do not use calculator.

(1) Circle the correct option i.e. A/B/C/D. Each part carries one mark.

- (i) In the compound  $C_4H_8$ ,  $C_4H_{10}$ ,  $C_4H_6$ , which compound is not a hydrocarbon? (1 mark)
 

A.  $C_4H_8$  B.  $C_4H_{10}$  C.  $C_4H_6$  D. None
- (ii) Petroleum hydrocarbons are called: (1 mark)
 

A. Simple hydrocarbons B. Complex hydrocarbons C. Acyclic hydrocarbons D. Aromatic hydrocarbons
- (iii) ~~1~~ Which of the following is not a hydrocarbon? (1 mark)
 

A. Detection of double bonds B. Detection of triple bonds C. Detection of aromaticity D. Detection of unsaturation
- (iv) Electrolysis of acid concentrated sulphuric acid is used to produce: (1 mark)
 

A. Ethane B. Ethene C. Ethyne D. Ethanol
- (v) The marsh gas is: (1 mark)
 

A. Ethane B. Methane C. Propane D. Butane
- (vi) Acetylene gives: (1 mark)
 

A. White ppt. With  $AgNO_3$  and red ppt. With  $CaCl_2$  B. White ppt. With  $AgNO_3$  and red ppt. With  $CaCl_2$  C. White ppt. With both A and B D. No ppt. With both A and B
- (vii) Acidic hydrogen is present in: (1 mark)
 

A. Acetylene B. Ethane C. Ethene D. Ethanol
- (viii) ~~2~~ Which of the following product is obtained when methyl magnesium bromide reacts with acetone? (1 mark)
 

A. Acetone B. Methanol C. Methane D. Ethanol
- (ix) ~~3~~ Ethylene reacts with ozone in cold to give: (1 mark)
 

A. Formaldehyde B. Ethyl alcohol C. Ozonide D. Acetaldehyde
- (x) Presence of double or triple bond is sign of: (1 mark)
 

A. Unsaturation B. Saturation C. Aromaticity D. Aromaticity
- (xi) Addition of HCN to ethyne in the presence of  $Cu_2Cl_2$ ,  $NH_4Cl$  gives: (1 mark)
 

A. 1,1-dicyanoethane B. Ethynol C. Acetylenol D. Ethynol
- (xii) Which hydrocarbon is formed by action of sodium on ethyl iodide? (1 mark)
 

A. Methane B. Ethane C. Ethene D. Ethanol
- (xiii) ~~4~~ The product formed when acetylene is passed through red hot tube is: (1 mark)
 

A. Benzene B. Cyclohexane C. Acetylene D. Ethanol
- (xiv) Soda lime is: (1 mark)
 

A. NaOH B. KOH C. Mixture of NaOH and CaO D. CaO and NaOH
- (xv) ~~5~~ Vinyl acetylene combines with HCl to form: (1 mark)
 

A. Polyacetylene B. Ethyl acetylene C. Chloroacetylene D. Ethanol
- (xvi) ~~6~~ Mustard gas is a: (1 mark)
 

A. gas B. solid C. Highly soluble liquid D. None
- (xvii) To which of the following compounds addition of HCN will follow Markovnikov's rule? (1 mark)
 

A.  $CH_3CH=CHCH_3$  B.  $CH_3CH=CH_2$  C.  $CH_2=CH_2$  D. None

**SUBJECTIVE**

Total Marks Section B and C: 08

Section B: Marks 12 (14 x 3 = 42)

Time: 2:35 Hours

Q2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines.

- (i) In Ethyne and other terminal alkynes, H atom attached to the triple bonded carbon is called acidic. (1 mark)
  - a. Why 1-alkynes or Ethyne show acidic behaviour? (1 mark)
  - b. Write a reaction to show the acidic behaviour of Ethyne. (1 mark)
- (ii) Give mechanism of addition of bromine to double bond. (2 marks)
- (iii) a. Define Markovnikov's rule. (1 mark)
 

b. Complete the following reaction  $CH_3=CH-CH_3 + HBr$ . (1 mark)
- (iv) Both alkenes and alkynes are unsaturated hydrocarbons. (1 mark)
  - a. How will you differentiate between ethene and ethyne? Give your answer with the help of a suitable chemical reaction. (1 mark)
  - b. Explain why ethene is more reactive than ethane. (1 mark)
  - c. How does ethyne react with hydrogen? (1 mark)



- (iv) How is 2-Butene prepared from  
a. An alkyl halide      b. A vicinal dihalide      03
- (v) Briefly explain the difference between Lindlar's catalyst and Raney-Nickel catalyst with respect to their composition and use      03
- (vi) How will you convert  
a. Ethanol  $\rightarrow$  Ethene      b. Ethene  $\rightarrow$  Formaldehyde      1.5 + 1.5
- (vii) Halogenation is believed to proceed through free radical mechanism in alkanes  
a. Write the names of steps involved in this process with examples.      01  
b. Write the mechanism of methane with bromine.      02
- (ix) Complete the following using given hints  
a. propene  $\xrightarrow{\text{Br}_2}$  ?  $\xrightarrow[\text{Alcoholic}]{\text{KOH}}$  ?      01  
b. propyne  $\xrightarrow{\text{HCN}}$  ?  
c. Ethane  $\rightarrow$  Ethene  $\rightarrow$  Ethyne      (02)
- (x) a. Why alkanes are least reactive than alkenes?      1.5  
b. What are heat of hydrogenation?      1.5
- (xi) a. What is meant by decarboxylation give its one use?      02  
b. Write the structural formulas of following: (a) Vinyl bromide (b) isobutylene.      01
- (xii) a. What is the effect of branching on boiling point of alkanes?      01  
b. How many ethene be converted in to ethyl alcohol?      01  
c. Alkenes usually undergo addition reactions while alkanes do not why?      01
- (xiii) How does Ethyne react with  
a.  $\text{AgNO}_3 / \text{NH}_4\text{OH}$       b.  $\text{H}_2\text{O} / \text{H}_2\text{SO}_4, \text{HgSO}_4$       03
- (xiv) a. Justify the given order of reactivity in electrophilic addition reactions.  
Alkenes > alkynes      02  
b. What is conjugation.      01
- (xv) a. Why alkanes are called paraffins?      01  
b. Why alkenes are called olefins?      01  
c. What is meant by dehydration of alcohols?      01
- (xvi) a. How do you convert alkynes into cis and trans alkenes.      02  
b. What is Baeyer's reagent and Baeyer's test?      01
- (xvii) a. How will you distinguish between ethane and ethyne.      01  
b. How mustard gas is prepared.      01  
c. How will you distinguish between 1-butyne and 2-butyne by chemical test.      01
- (xviii) a. What is meant by optical activity?      01  
b. What is tautomerism? Give examples.      02
- (xix) a. How aldehydes or ketones are produced from alkenes?      02  
b. What is a polymerization reactions?      01

### Section - C

**Note:** Attempt any TWO questions. All questions carry equal marks. (2  $\times$  13 = 26)

- Q. 3.** a. How will you prepare 1-butene from?      03  
(i) An alkyl halide (ii) Alcohols

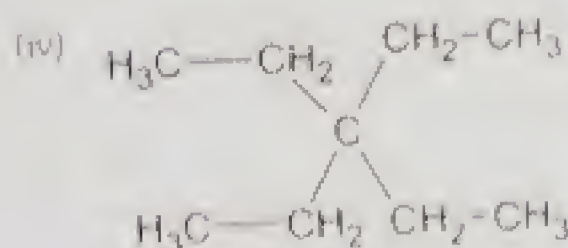
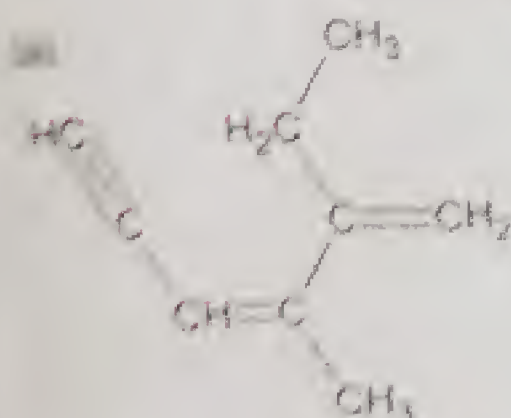
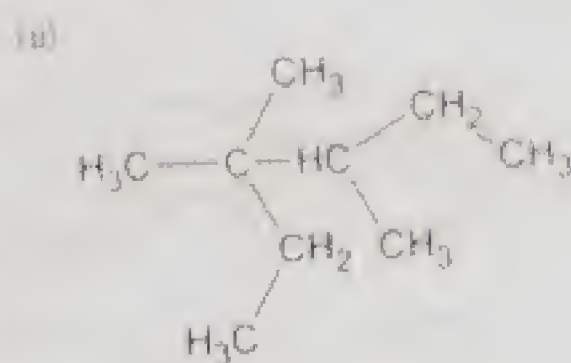
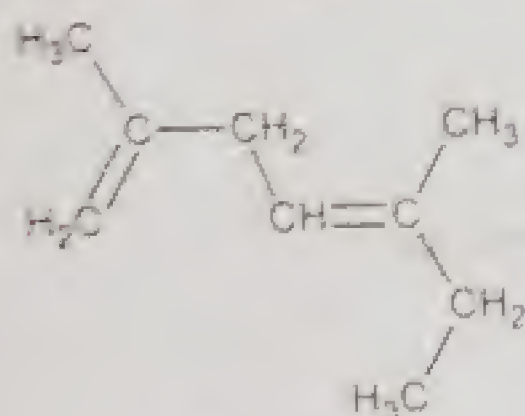


Q 8. (a) Methacarbonic

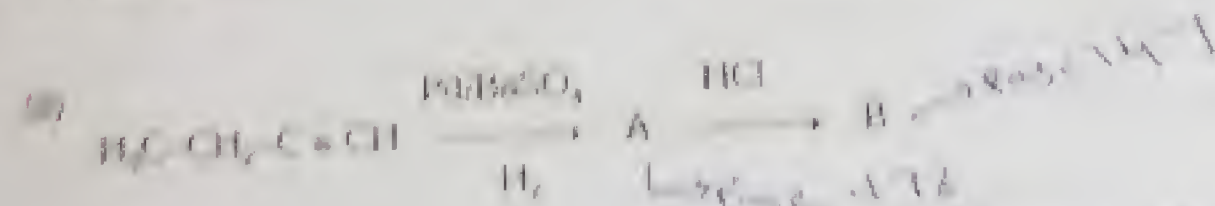
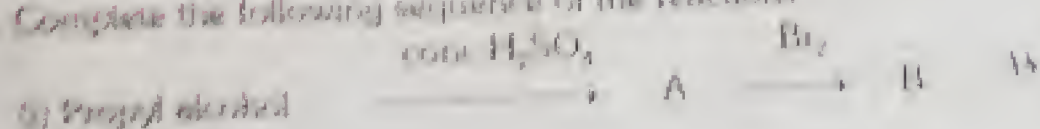
8. How will you prepare the following compounds from ethyne? (i) Acetaldehyde (ii) Benzene (iii) a geminal dihalide (iv) Ethane (v) tetrahalide  
 9. A compound 'X' when treated with Zn in methanol, the alkene is formed. When alkene is ozonolyzed the acetaldehyde is formed as major product. Explain reactions involved, give name and structure of this compound 'X'.  
 10. Define configuration.

4. (a) What is Raney nickel? Give some examples in which it is used as catalyst.  
 (b) Write mechanism of addition of HBr to propene.  
 (c) Write the complete reaction when aqueous  $\text{Cl}_2$  is added to an alkene.  
 (d) Give preparation of ethene by:  
 (i) Dihydrohalogenation of vicinal dihalide  
 (ii) Dissolving metal reduction.

9. (a) Give the IUPAC names to the following compounds.



10. Complete the following sequence of the reactions



11. How the alkenes are polymerized? Explain with example.  
 12. How does cis isomer convert into trans isomer?



## TEST YOUR SKILLS

## (AROMATIC COMPOUNDS)

## OBJECTIVE

Time: 20 Minutes

Marks: 17

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Q1. Circle the correct option i.e. A/B/C/D. Each part carries one mark.

- (i) The conversion of n-hexane into benzene by heating in the presence of Pt is called  
A. isomerism **B. aromatization** C. dealkylation D. rearrangement
- (ii) Catalyst used for Friedel craft's reaction is  
A.  $\text{HNO}_3$  **B.  $\text{AlCl}_3$**  C.  $\text{BeCl}_2$  D.  $\text{NaCl}$
- (iii) Benzoic acid formed by oxidation of  
A. Toluene B. Ethyl benzene C. n-propyl benzene **D. All**
- (iv) C-C bond length in benzene is  
A. 1.34 Å B. 1.20 Å **C. 1.40 Å** D. 1.54 Å
- (v) Aromatic compounds burn with soot flame because  
A. High percentage of hydrogen B. Ring structure  
**C. High percentage of carbon** D. They resist reaction with air
- (vi) Resonance structure of a molecule should have  
A. Same number of paired electrons B. Identical arrangement of atoms  
C. Nearly same energy content **D. All of these**
- (vii) In which one of the following compounds the benzene rings are isolated  
A. Naphthalene B. Anthracene C. Phenanthrene **D. Diphenyl methane**
- (viii) Benzene can not undergo  
**A. Elimination** B. Substitution C. Oxidation D. Addition
- (ix) Nitrating agent in nitration of benzene is  
A.  $\text{HNO}_3$  **B.  $\text{NO}_2^+$**  C.  $\text{NO}_3^-$  D.  $\text{NO}_2^-$
- (x) Benzene on catalytic oxidation at  $500^\circ\text{C}$  with  $\text{V}_2\text{O}_5$  as catalyst gives  
A. Benzoic acid **B. Maleic anhydride** C. Maleic acid D. Acetylene
- (xi) Amongst following, strongest o,p-directing group is  
A.  $-\text{Cl}$  **B.  $-\text{OH}$**  C.  $-\text{C}_6\text{H}_5$  D.  $-\text{Br}$
- (xii) The effect of substituent Cl in electrophilic substitution reactions is  
**A. o,p-director and deactivating** B. o,p-director and activating  
C. m-director and activating D. m-director and deactivating
- (xiii) The aromatic ring can be hydrogenated by using the catalyst  
**A. Pt** B. Pd C. Rh D. None
- (xiv) Which xylene gives only one monobromo derivative?  
**A. Para** B. Meta C. Ortho D. None
- (xv) Benzene is prepared from cyclohexane by the process called  
A. Hydrogenation B. Dehydration **C. Dehydrogenation** D. None of these
- (xvi) In which one of the following compounds the nitration is difficult  
A. Toluene **B. Nitrobenzene** C. Benzene D. Phenol
- (xvii) Shape of benzene molecule is  
A. Pyramidal B. Linear Plane C. trigonal **D. hexagonal Planar**

## SUBJECTIVE

Time: 2:35 Hours

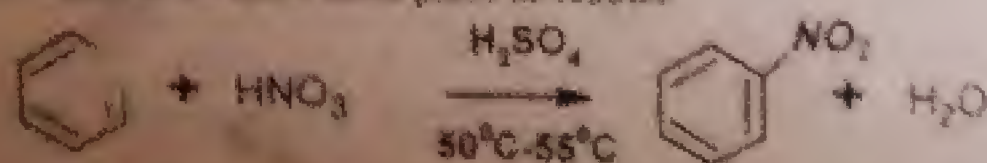
Total Marks Section B and C: 68

Section - B (Marks 42) ( $14 \times 3 = 42$ )

Q2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines.

- (i) The carbon-carbon bond length in Benzene is different from that in Ethene  
a. Which compound contains the longer bond?  
b. Give reason for your answer
- (ii) Aromatic compounds undergo Electrophilic Substitution reactions  
a. Explain why Nitration of Toluene is easier than that of Benzene  
b. How would you convert Toluene into Trinitrotoluene (TNT)?

(iii) Nitration of benzene takes place as follows:



- a. Which is the nitrating agent and how it is generated?  
b. Write complete mechanism for the above conversion upto the formation of arenium ion.



**Chapter: Hydrocarbons**

- (vi) Benzene is an extraordinary stable molecule. Justify the truth with the help of example
- How can benzene be converted into acetophenone? 01
  - How can aniline be converted into benzene? 02
- (vii) Complete the following reactions with mechanism.
- $C_6H_6 + SO_3 \xrightarrow{H_2SO_4} ?$  1.5
  - $C_6H_6 + CH_3COCl \xrightarrow{AlCl_3} ?$  1.5
- (viii) a. What are aromatic hydrocarbons? 01
- What are monocyclic and polycyclic aromatic hydrocarbons? 01
  - What are aryl groups? 01
- (ix) a. Give reactions, which show that benzene has a cyclic structure with three alternate double bonds. 02
- Why Kekule's formula was rejected? 01
- (x) a. Why Kekule's structure has greater contribution towards the actual structure of benzene? 02
- How resonance energy is related to the stability of molecule? 01
- (xi) a. Why carbon-carbon bonds are of equal length in benzene? 01
- Give two reactions, which shows that benzene is a saturated compound. 02
- (xii) a. Benzene usually undergoes electrophilic substitution reaction and not addition reaction, why? 02
- What product will be formed, when benzene react with  $Cl_2$  in the presence of sunlight? 01
- (xiii) a. Write the mechanism of alkylation of benzene. 1.5
- Nitration of toluene gives *ortho* and *para* nitrotoluene while nitration of nitrobenzene gives meta-dinitro benzene. Explain? 1.5
- (xiv) a. What products are formed by the oxidation of toluene and ethyl benzene? 01
- Why nitrobenzene is less reactive than benzene towards electrophiles? 01
  - What is Friedel-Craft acylation reaction? 01
- (xv) a. How will you obtain maleic acid from benzene? 01
- Give general mechanism of electrophilic substitution reaction of benzene. 02
- (xvi) a. What are Friedel and Craft reactions? 01
- Write down IUPAC name of *o*-xylene and *p*-xylene? 01
  - Why Dewar structures of benzene are considered as unstable? 01
- (xvii) a. How benzene is obtained from A. acetylene B. n-hexane 02
- Give all possible isomers of xylenes. 01
- (xviii) a. Justify the given order of reactivity Alkenes > Benzene > Alkanes 1.5
- What information was obtained from X-ray analysis of benzene? 1.5
- (xix) a. What are isolated and fused polycyclic hydrocarbons? Give examples. 02
- What is Robinson structure of benzene? 01

**Section - C**

**Note:** Attempt any TWO questions. All questions carry equal marks. (2 × 13 = 26)

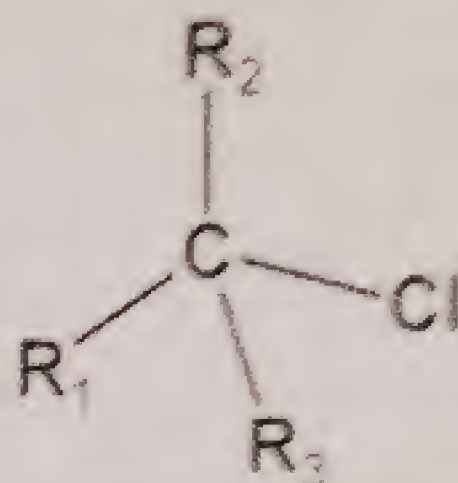
- Q. 3.** a. How will you prove that benzene has cyclic structure? 03
- Explain the structure of benzene according to Atomic orbital treatment. 04
  - Why benzene is stable compound? Explain with facts. 04
  - How will you prepare benzene from? 04
- Alkanes
  - Phenol
  - Salt of benzoic acid
- Q. 7.** a. Explain the following electrophilic substitution reactions of benzene with mechanism. 06
- Halogenation
  - Sulphonation
  - Friedel craft acylation
- Draw the structural formulas for the following compounds. 05
- p*-Chlorobenzoic acid
  - m*-Dinitrophenol
  - p*-Dibenzyl benzene
  - Benzoyl chloride
  - p*-Aminophenol
- Name four *meta*-directing groups. 02
- Q. 8.** (a) What products are formed when benzene reacts with? 04
- $Br_2$  in presence of sunlight
  - $O_2$
  - $O_3$
  - $H_2/Pt$
- Explain that how *ortho* and *para*-directing groups affect the reactivity of benzene? 03
  - Define Resonance. Draw all the possible resonating structures shown by a benzene. 06
  - What structure would you suggest best for representing benzene?





## CHAPTER # 17

# ALKYL HALIDES AND AMINES



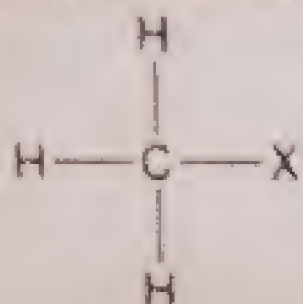
## ALKYL HALIDE

### INTRODUCTION

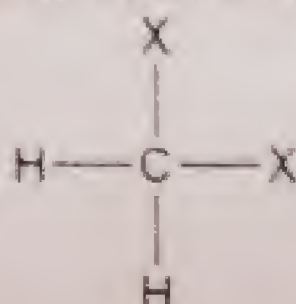
Alkyl halides are the compounds in which one hydrogen atom of Alkanes has been replaced by a halogen atom. They are also known as halogen derivatives."

### TYPES:

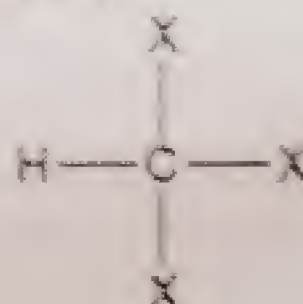
They may be Mono, di, tri or poly haloalkanes depending upon the number of halogen atoms present in the molecule. Monohaloalkanes are called alkyl halides. These have general formula  $R-X$ .



Monohaloalkane



Dihaloalkane



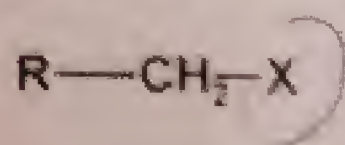
Trihaloalkane

## CLASSIFICATION OF ALKYL HALIDES

Alkyl halides are classified into primary, secondary and tertiary alkyl halides.

### (i) Primary Alkyl Halides:

Alkyl halide in which halogen atom is attached with primary carbon are called primary halides. A primary C-atom is attached to one or no carbon atom is called a primary C-atom.



Methyl chloride



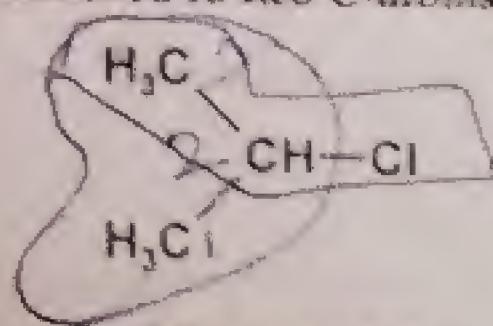
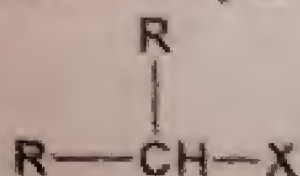
Ethyl chloride



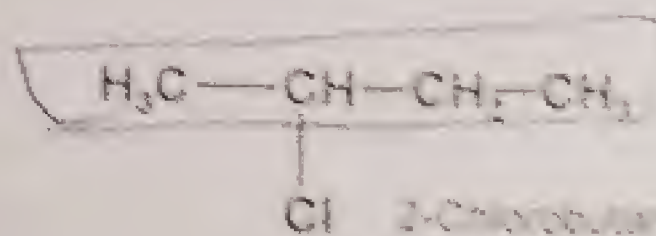
n-Propyl chloride

### (ii) Secondary Alkyl Halides:

Alkyl halide in which halogen atom is attached with a secondary carbon atom is called secondary alkyl halide. A Secondary C-atom is attached to two C-atoms simultaneously is called a secondary C-atom.



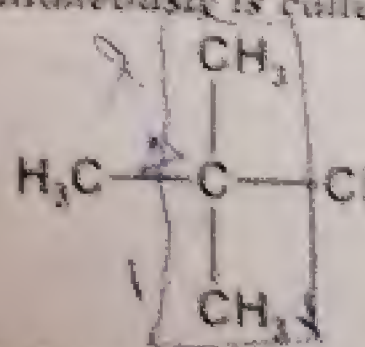
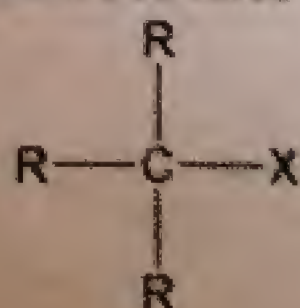
2-Chloropropane



2-Chlorobutane

### (iii) Tertiary Alkyl Halides:

Alkyl halides, in which halogen atom is attached to a tertiary carbon is called tertiary alkyl halide. A tertiary C-atom is attached to three C-atoms simultaneously is called a tertiary C-atom.



2-Chloro-2-methylpropane



## NOMENCLATURE

Alkyl halides are named according to the following systems.

(i) Common System of naming (ii) IUPAC System of naming

### (i) Common System of Naming:

- First write the name of alkyl group to which halogen atom is attached and then write the name of halide ion.
- For secondary alkyl halides, the prefix *sec-* and for tertiary alkyl halides, the prefix *ter-* is added before the name of alkyl halide e.g.,
- When all the carbons of alkyl group of primary alkyl halides are in a straight chain, the prefix *n-* is used before the name which indicates 'normal'. The prefix *iso-* is used for branched alkyl group having methyl group on second last carbon atom.

#### Examples:



Methyl chloride



Ethyl chloride



n-Propyl chloride



isopropyl chloride or  
isobutyl chloride



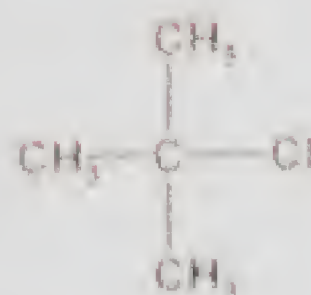
n-Butyl chloride



sec-Butyl chloride



isobutyl chloride



tert-butyl chloride

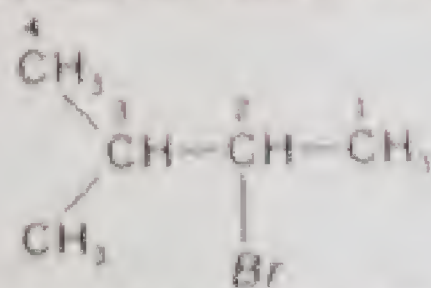
### (ii) IUPAC System of naming

According to this system alkyl halides are named as derivatives of Alkane. The rules are:

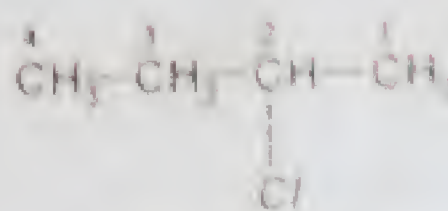
- The longest chain bearing halogen is selected as parent hydrocarbon.
- Prefix 'halo' i.e., chloro for Cl, Bromo for Br, etc. is used before the name of hydrocarbon.
- Positional numbers are used to indicate halogens and other substituents by the usual methods.



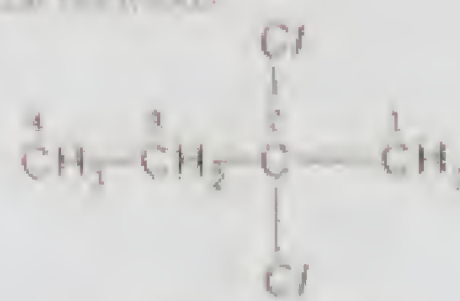
1-Chloropropane



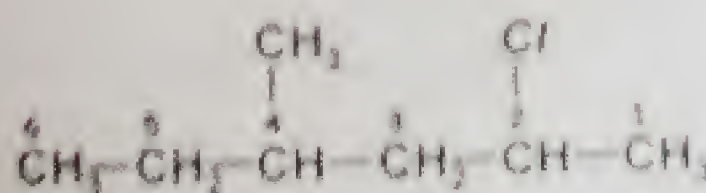
2-Bromo-3-methylbutane



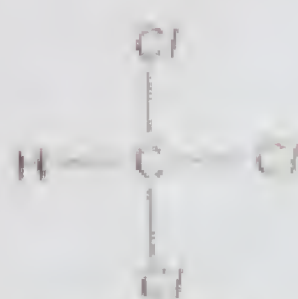
1-Chlorobutane



2,2-Dichlorobutane



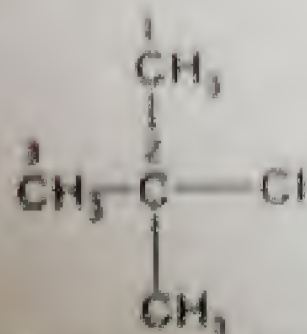
2-Chloro-4-methylhexane



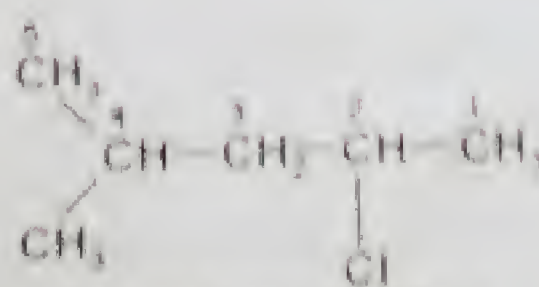
trichloromethane



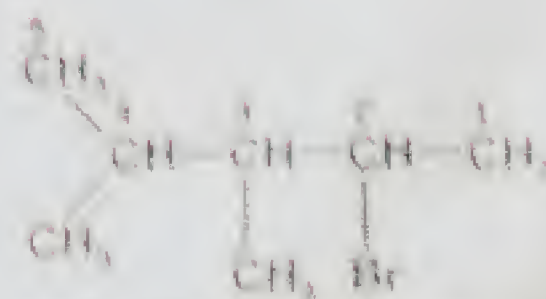
tetrachloromethane



2-Chloro-2-methylpropane



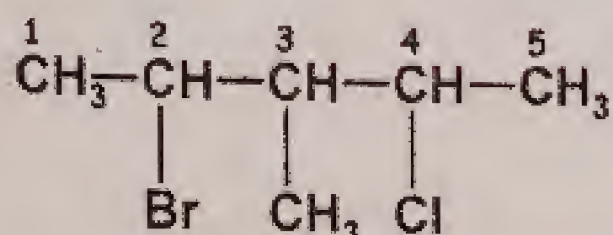
2-Chloro-4-methylpentane



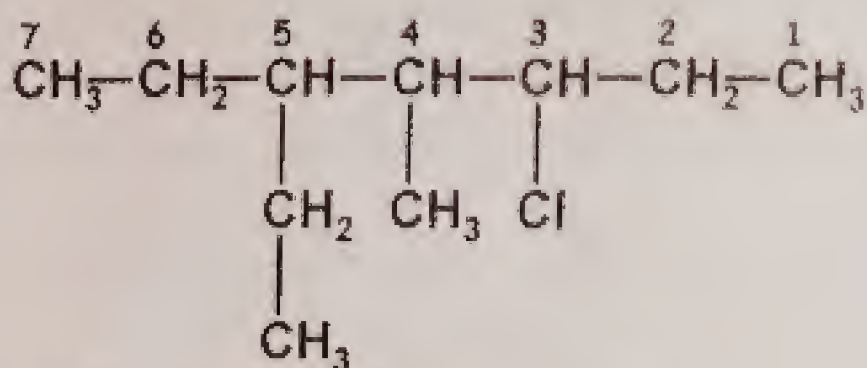
3-Bromo-5,5-dimethylpentane



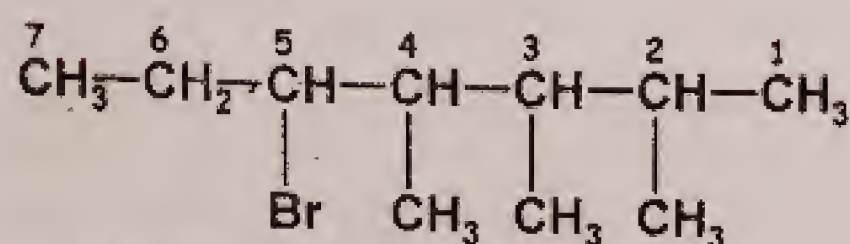
**MORE PRACTICE**



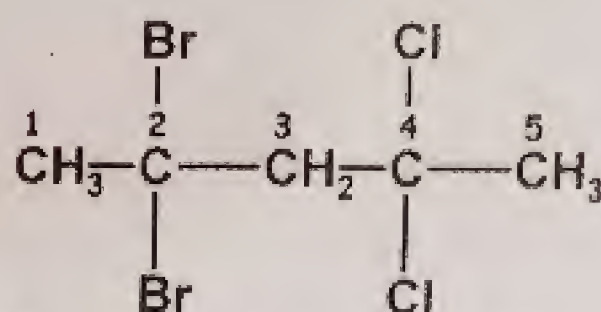
2-Bromo-4-chloro-3-methylpentane



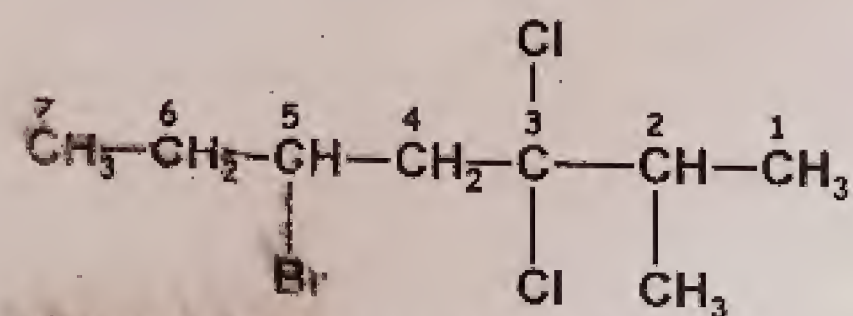
3-Chloro-5-ethyl-4-methylheptane



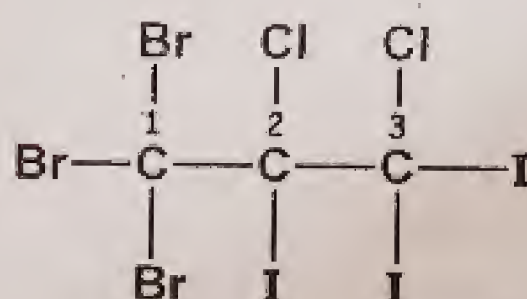
5-Bromo-2,3,4-trimethylheptane



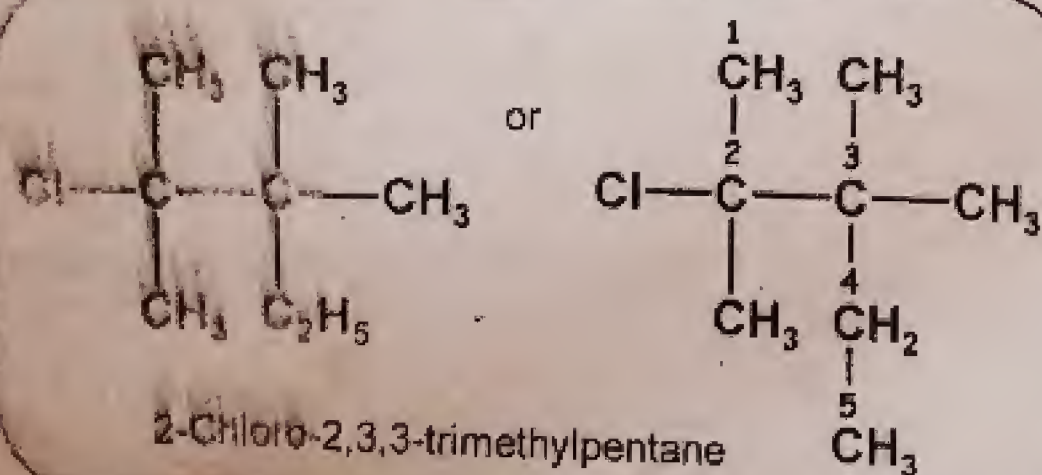
2,2-Dibromo-4,4-dichloropentane



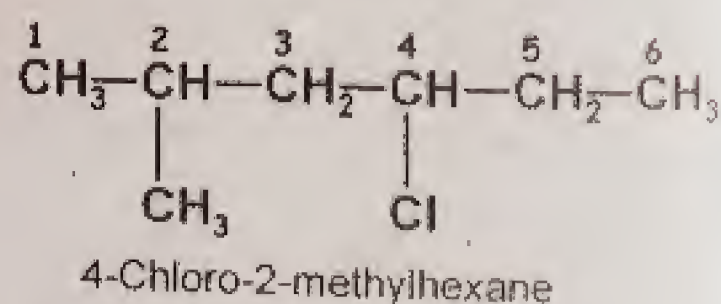
5-Bromo-3,3-dichloro-2-methylheptane



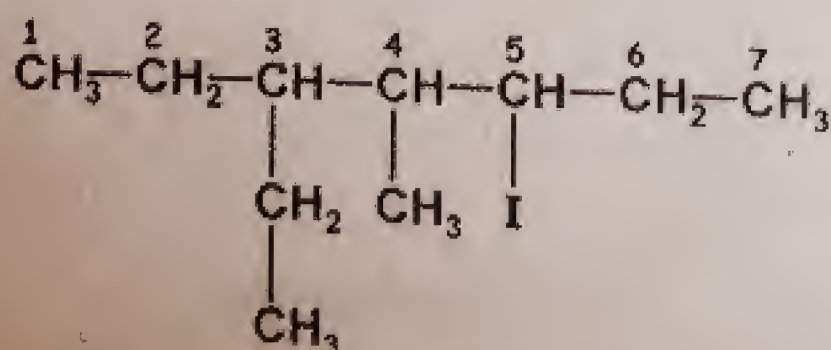
1,1,1-Tribromo-2,3-dichloro-2,3,3-triiodopropane



2-Chloro-2,3,3-trimethylpentane

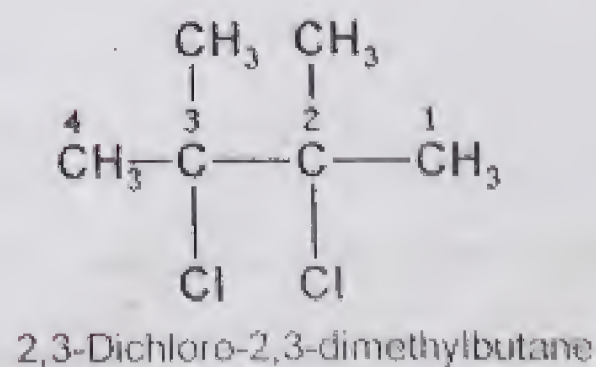
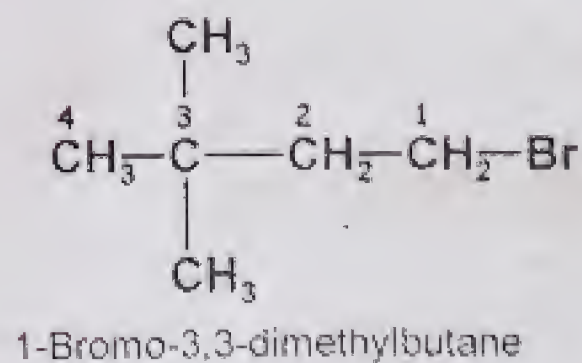
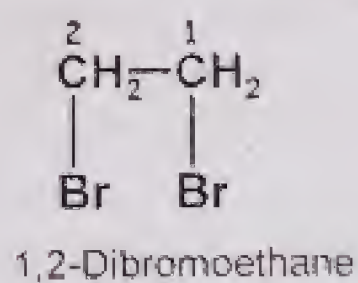
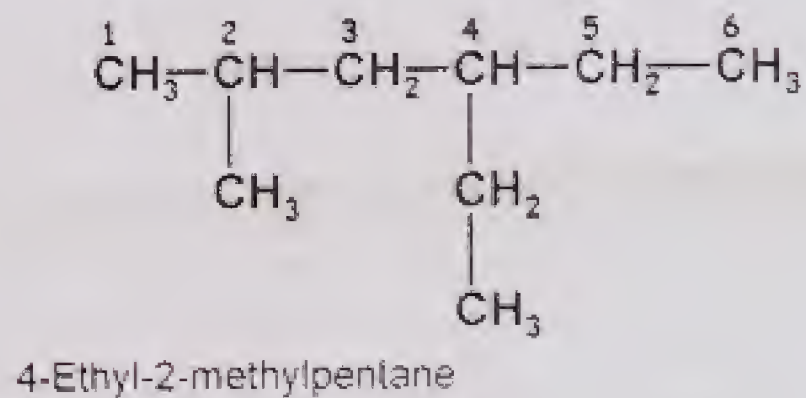
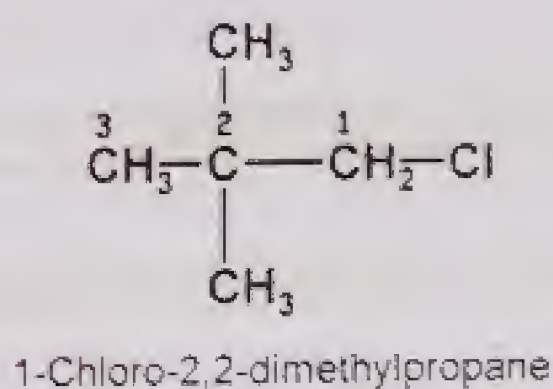
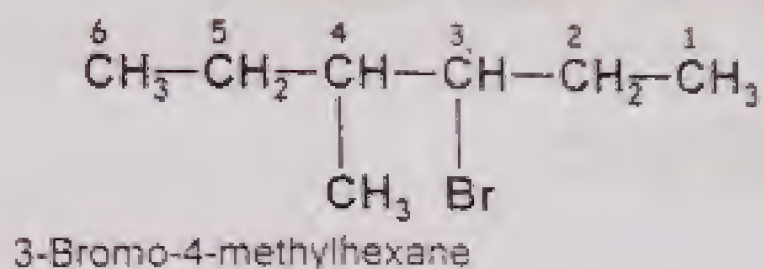
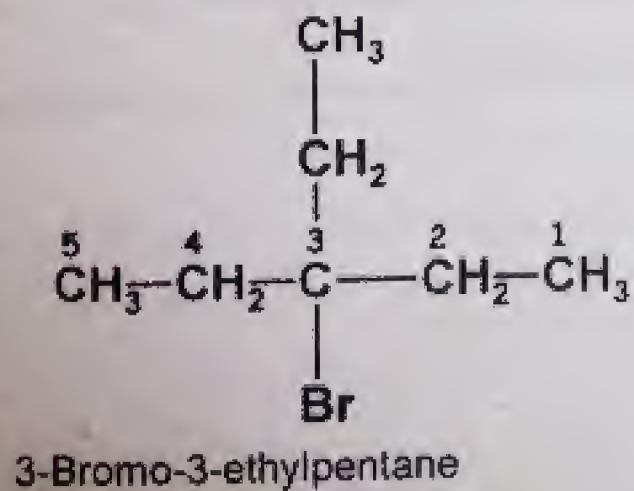
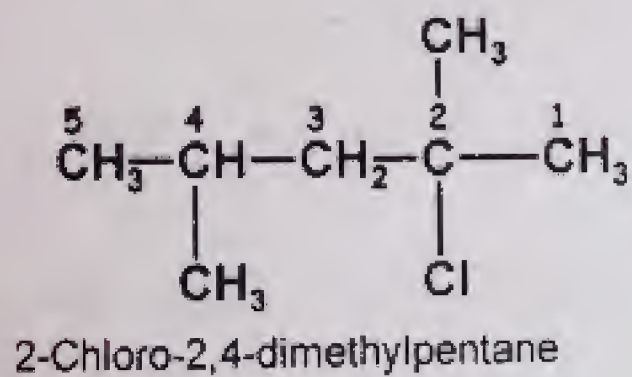
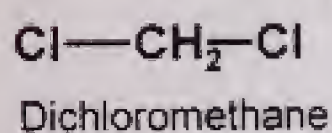
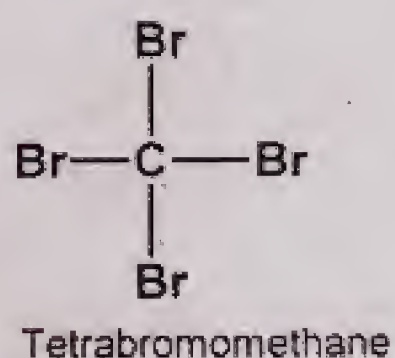
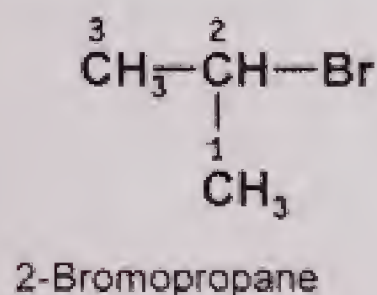
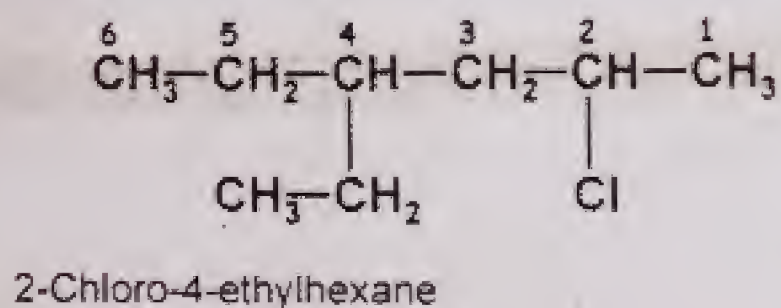
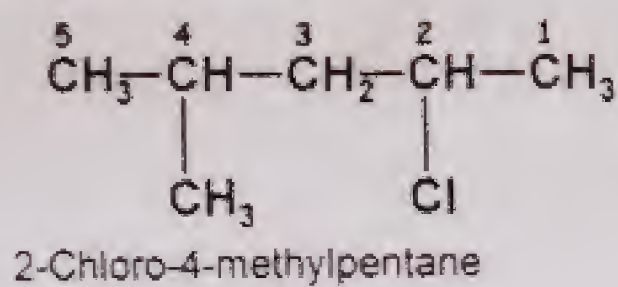


4-Chloro-2-methylhexane



3-Ethyl-5-iodo-4-methylheptane







**PHYSICAL PROPERTIES**

The alkyl halides contain a polar bond. Thus, it has higher melting points and boiling points than alkanes.

**STRUCTURE**

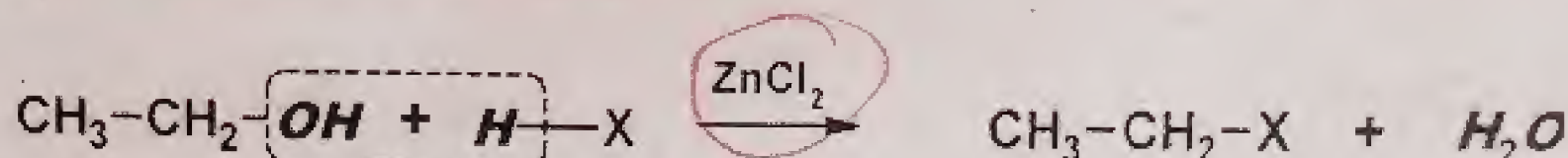
- The alkyl halide functional group consists of an  $sp^3$ -hybridized C atom bonded to a halogen atom (X) by a  $\sigma$ -bond.
- The carbon halogen bonds are polar due to the electronegativity and polarizability of the halogens.

**PREPARATIONS OF ALKYL HALIDES**

**Exercise Q3 (ii)** Give three methods for the preparation of alkyl halides.

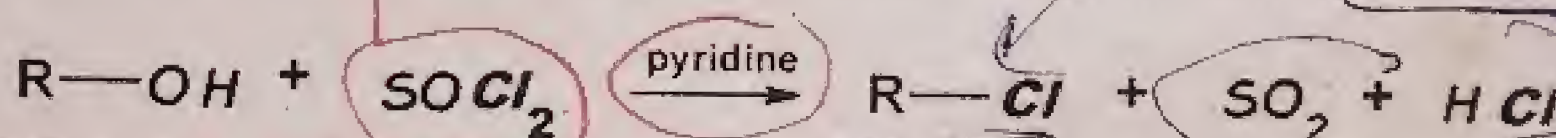
**(1) Reaction of Alcohols with Hydrogen Halides**

Alcohols may be converted to the corresponding alkyl halides by the action of halogen acid in the presence of  $ZnCl_2$  as a catalyst.

**(2) Reaction of Alcohols with other Halogenating agents ( $SOCl_2$ ,  $PX_3$ )**

(a) Alcohols react with thionyl chloride in pyridine as a solvent to give alkyl chlorides.

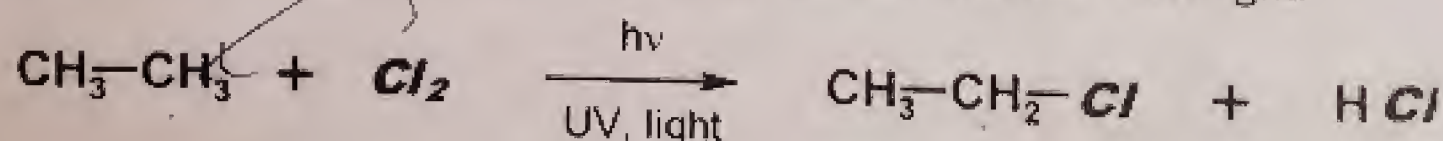
This is the best method because HCl and  $SO_2$  are gases which escape out leaving behind the pure product.



(b) Phosphorous trihalides or phosphorous pentahalides react with alcohols to form alkyl halides.

**(3) Halogenation of Alkanes**

- Alkanes react with chlorine or bromine to give alkyl halides.
- This reaction takes place in the presence of diffused sunlight or ultraviolet light.

**NOTE:**

- This method does not give pure alkyl halides. Halogen derivatives containing two or more halogen atoms are also formed along with alkyl halides.

The detail mechanism of this reaction has already been discussed in Chapter # 16 (Radical Substitution Reactions).

**REACTIVITY**

**Exercise Q3 (i)** Discuss the reactivity of alkyl halides.

There are two main factors which control the reactivity of alkyl halides:

- (1) Bond polarity of C-X bond
- (2) Bond energy of C-X bond



### 1. Bond Polarity

- The molecule of alkyl halide is polarized due to the greater electronegativity of halogens as compared to C.

Atom	Electronegativity	Atom	Electronegativity
F	4.0	I	2.5
Cl	3.0	H	2.1
Br	2.8	C	2.5

- Hence carbon acquires partial positive whereas halogens acquires partial negative charge ( $\overset{\delta+}{\text{C}}-\overset{\delta-}{\text{X}}$ )
- Halogen becomes nucleophilic in character, which can be replaced by another nucleophile.
- The polarity order is  $\text{R-F} > \text{R-Cl} > \text{R-Br} > \text{R-I}$

### 2. Bond Energy

- Experiments have shown that the bond energy of C-X bond is the main factor which decides the reactivity of alkyl halides, and not the polarity of the molecule.
- A study of bond energies of C-X bond shows that C-F bond is the strongest. So the overall order of reactivity of alkyl halides is:

$\text{R-iodide} > \text{R-bromide} > \text{R-chloride} > \text{R-fluoride}$

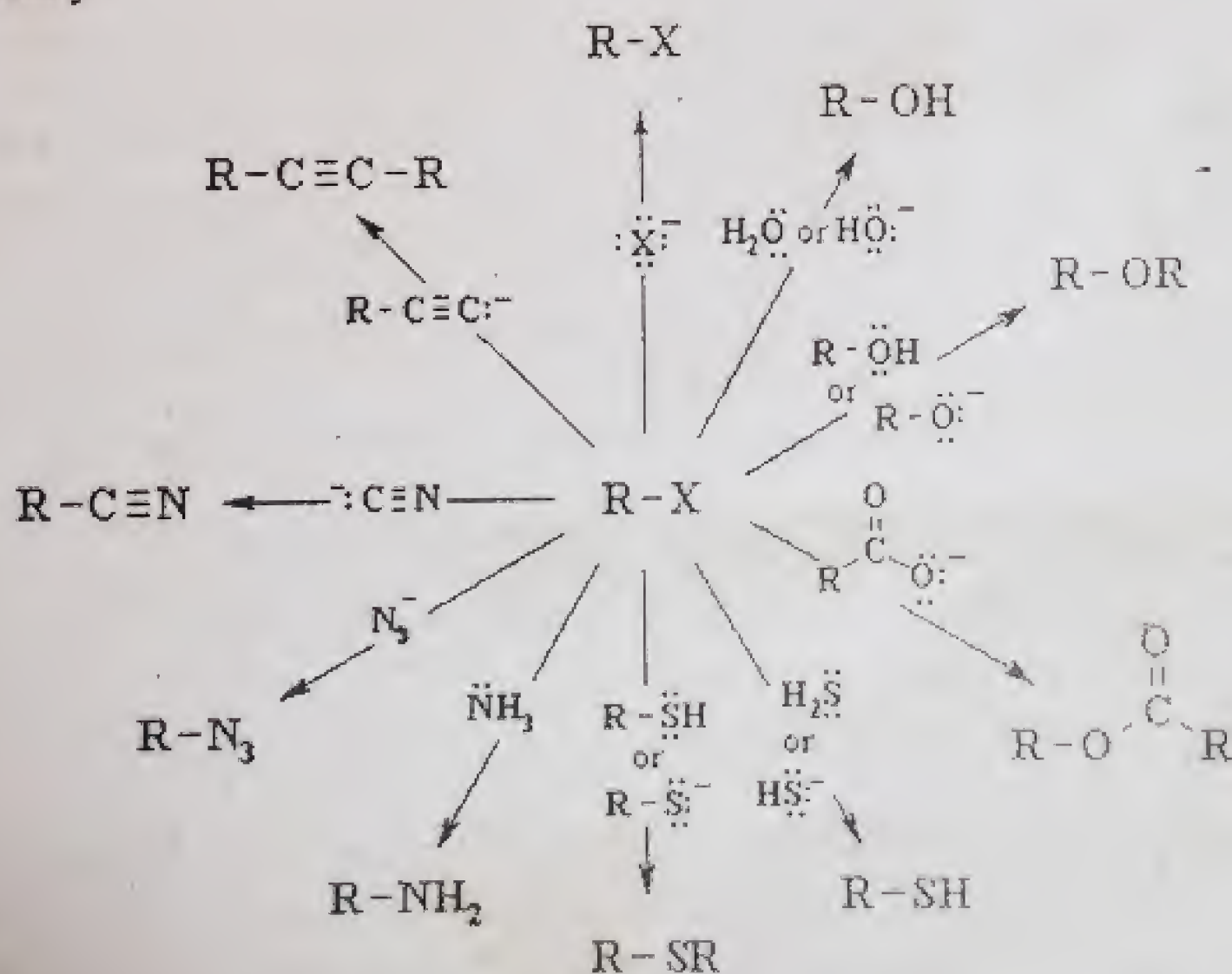
- In fact the C-F bond is so strong that alkyl fluorides do not react under ordinary conditions.

more stable, the less react it will be.

### NUCLEOPHILIC SUBSTITUTION REACTIONS OF ALKYL HALIDES

- Alkyl chlorides, bromides and iodides are good substrates for substitution reactions.
- A variety of nucleophiles can be used to generate a range of new functional groups.
- The following diagram reflects some of the more important reactions you may encounter.
- For practice, make sure you can draw the mechanisms that lead to these products.

#### Reactions Summary





## IMPORTANT DEFINITIONS

### Electrophile

Species in search of negative charge is called an electrophile

#### Examples

$\text{NO}_2^+$ ,  $\text{Br}^+$ ,  $\text{CH}_3^+$  etc.

### Nucleophile

Species in search of positive charge is called a nucleophile

OR A nucleophile is electron rich species that will react with an electron poor species. It has a lone pair of electrons available for bonding or has negative charge.

#### Examples

$\text{HO}^-$	Hydroxide ion	$\text{NH}_2^-$	Amino group
$\text{C}_2\text{H}_5\text{O}^-$	Ethoxide ion	$\text{Cl}^-$	Chloride ion
$\text{HS}^-$	Hydrogen Sulphide ion	$\text{Br}^-$	Bromide ion
$\text{SCN}^-$	Thiocyanate ion	$\text{NH}_3$	Ammonia
$\text{H}_2\text{O}$	Water		

### Substitution Reaction

A substitution is the reaction in which one group replaces another.

## NUCLEOPHILIC SUBSTITUTION REACTION

The reaction in which a nucleophile replaces another atom or a group of atom already present in molecule are called nucleophilic substitution reactions.

In these reactions, an electron rich species, the nucleophile, reacts at an electrophilic C atom attached to electronegative group, the leaving group, which is replaced.



- The electrophilic C is present in the polar sigma bond due to the presence of an electronegative substituent (e.g., C-Cl, C-Br, C-I and C-O)
- Nucleophilic substitution reactions allow the interconversion of functional groups.

## TYPES OF NUCLEOPHILIC SUBSTITUTION REACTION

There are two fundamental events in a nucleophilic substitution reaction:

- formation of the new  $\sigma$ -bond to the nucleophile
- breaking of the  $\sigma$ -bond to the leaving group

Depending on the relative timing of these events, two different mechanisms are possible:

- First old bond breaks and then new bond is formed:  $\text{S}_\text{N}1$  reaction
- Simultaneous bond formation and bond breaking:  $\text{S}_\text{N}2$  reaction

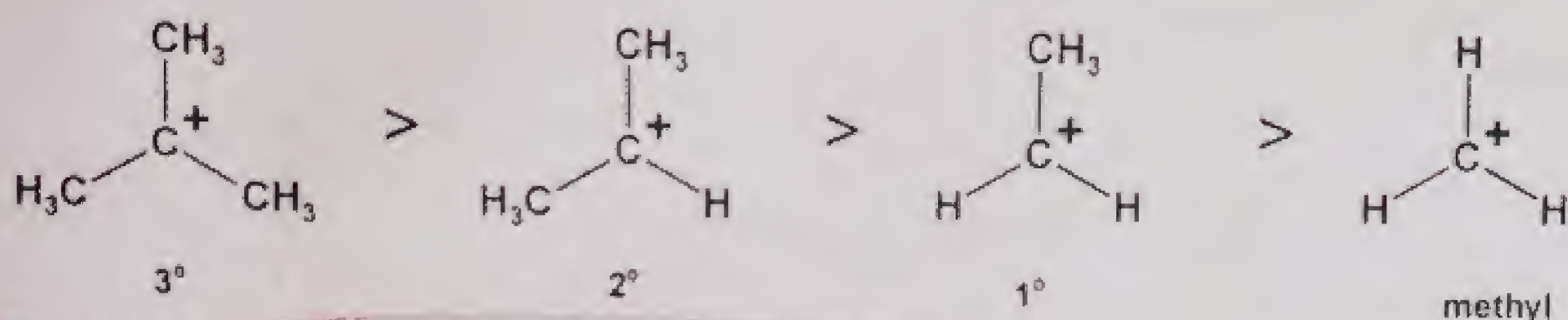


## CARBOCATIONS AND THEIR STABILITY

The ion with trivalent carbon and have positive charge on carbon atom is called a carbocation.

Stability:

- The general stability order of simple alkyl carbocations is: (most stable)  $3^\circ > 2^\circ > 1^\circ > \text{methyl}$  (least stable)



- This is because alkyl groups are weakly electron donating due to hyperconjugation and inductive effects. So, due to electron donating effect, they stabilize the positive charge on carbon atom.
- Since, tertiary carbocation has more alkyl groups attached to the positive carbon atom, so, it will be more stabilized than secondary carbocation and so on.
- Resonance effects can further stabilize carbocations when present. (For Resonance Effect see page 215)

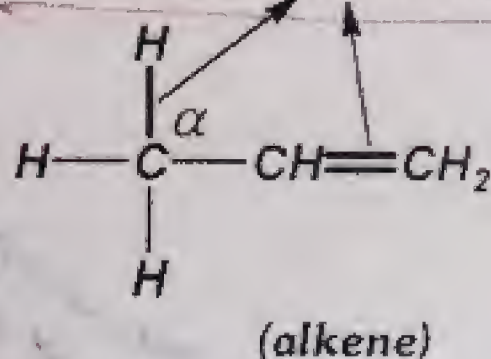
## SOME EXPLANATIONS

### Hyperconjugation

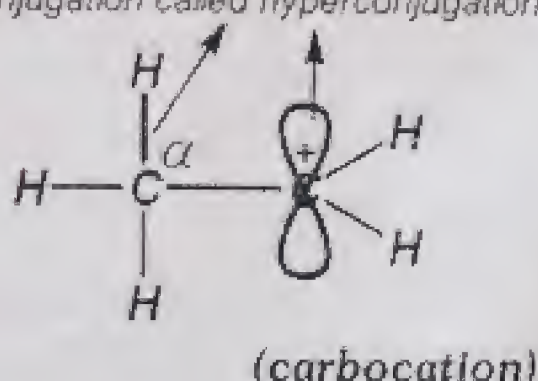
The conjugation of  $\sigma$  - electrons of a C - H bond with p - electrons of the unsaturated system or with p - orbital is called hyperconjugation.

Examples:

C-H bond and Double bond are in conjugation called hyperconjugation



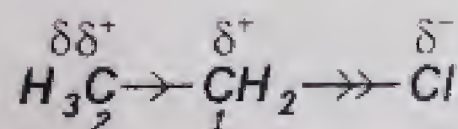
In carbocation, C-H bond and p-orbital on carbon with positive charge are in conjugation called hyperconjugation.



### Inductive Effect

The polarization of a bond induced by an adjacent polar bond is known as the Inductive Effect.

Example



In ethyl chloride, the more electronegative chlorine atom pulls shared electron towards itself. Thus, it gets  $\delta^-$  charge and C-1 gets  $\delta^+$  charge. The C-1 in turns pulls electrons from C-2. Thus C-2 also gets slight  $\delta\delta^+$  charge. However, charge on C-2 is less than C-1 because pull decreases along the chain.



**REACTIONS INVOLVING CARBOCATIONS**

1. Substitutions via the  $S_N1$
2. Eliminations via the  $E1$
3. Additions to alkenes and alkynes ( $HX$ ,  $H_2O^+$ )

**NUCLEOPHILES AND BASE**

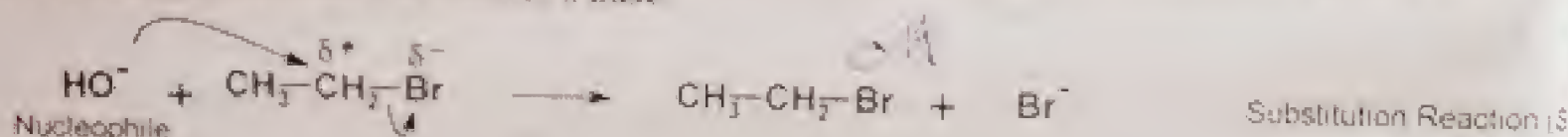
It is species rich in electron and has an unshared pair of electrons available for bonding.

- In most cases it is basic
- It may be negatively charged or neutral

**Examples**

$HO^-$	Hydroxide ion	$NH_3$	Amino group
$C_2H_5O^-$	Ethoxide ion	$Cl^-$	Chloride ion
$HS^-$	Hydrogen Sulphide ion	$Br^-$	Bromide ion
$SCN^-$	Thiocyanate ion	$NH_3$	Ammonia
$H_2O$	Water		

Generally, if a species rich in electron attacks on carbon atom, it is called as a **nucleophile**. However, if it attacks on a hydrogen atom then it is called as a **base**.

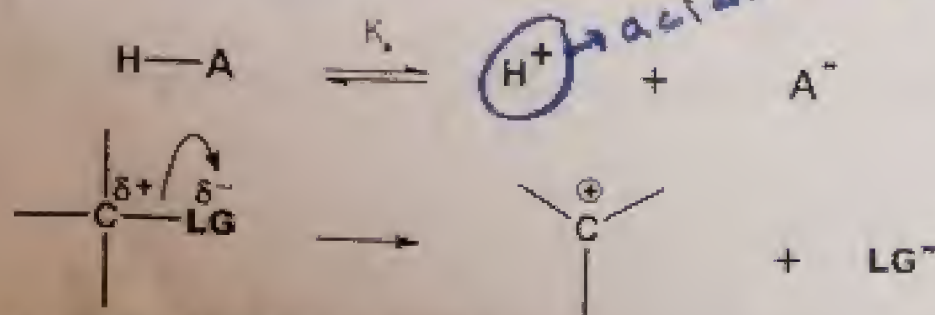
**SUBSTRATE AND LEAVING GROUP****SUBSTRATE MOLECULE**

The alkyl halide molecule on which a nucleophile attacks is called a substrate molecule.

**LEAVING GROUP (LG)**

Leaving group is also a nucleophile. It leaves with an unshared pair of electrons.

- The incoming nucleophile must be stronger than the leaving group.
- Good Leaving Groups are  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $HSO_4^-$ .
- Poor leaving groups are  $OH^-$ ,  $OR^-$  and  $NH_2^-$ .
- Iodide ion is a good nucleophile as well as a good leaving group.



Both these process are similar as both involves ionization.

- The first reaction represents the **Bronsted acid dissociation**.
- The second reaction represents the loss of a leaving group in an  $S_N1$  type reaction.

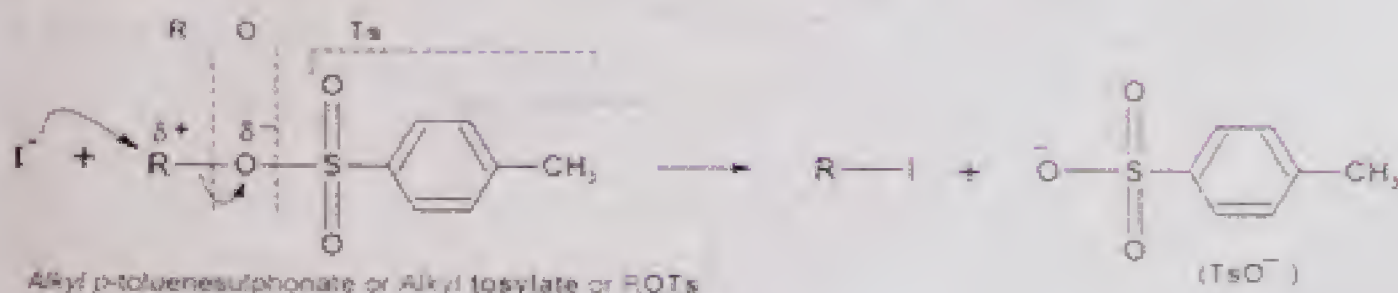


- Both these equations appear similar. Both show heterolytic cleavage of a C—Br bond to create an alkene and a carbocation.
- For alkyl, the more stable the alkyl R, the more the equilibrium will go in forward direction and hence dissociation. Thus, more release of bromide means that RBr is more acidic.
- For the leaving group, the more stable the LG, the more the reaction goes in forward direction and hence leaving.
- Hence factors that stabilize R<sup>+</sup> also apply to the stability of a LG. The leaving group can be classified as follows:

Excellent	TsO <sup>-</sup> , HSO <sub>4</sub> <sup>-</sup>
Very Good	F <sup>-</sup> , HClO <sub>4</sub>
Good	Br <sup>-</sup>
Fair	I <sup>-</sup>
Poor	Cl <sup>-</sup>
Very Poor	H <sub>2</sub> O, NH <sub>3</sub> , ROH

*Handwritten note: M.C.*

But water itself, H<sub>2</sub>O, is a good leaving group, since it's the conjugate base of H<sub>3</sub>O<sup>+</sup>. TsO<sup>-</sup> is excellent leaving group.



**Exercise Q3 (iii)** Explain in detail S<sub>N</sub>1 and S<sub>N</sub>2 reactions with mechanism.

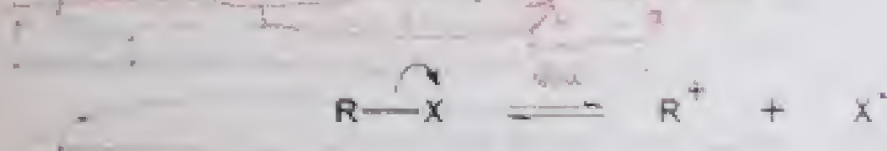
### S<sub>N</sub>1 MECHANISM

It is substitution nucleophilic unimolecular two step reaction.

#### **EXPLANATION:**

It takes place in two steps.

**Step-I:** The substrate R-X first ionizes reversibly into R<sup>+</sup> and X<sup>-</sup> ions.



**Step-II:** Then the carbocation combines with the attacking nucleophile to form product.



- Since only one molecule is undergoing a change in covalency in the rate determining step, therefore, it is a two step, unimolecular nucleophilic substitution reaction.



**EVIDENCES OF  $S_N1$  MECHANISM:****(1) Kinetic Evidence:**

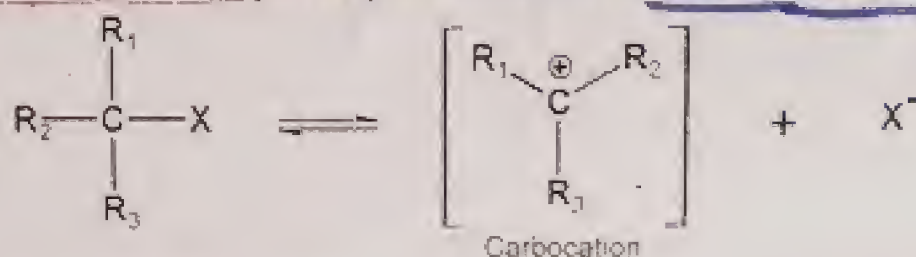
- The rate of an  $S_N1$  reaction depends upon the concentration of alkyl halide only.
- The change in concentration of attacking nucleophile has no effect on the rate. Thus

$$\text{Rate} = k[R-X]$$

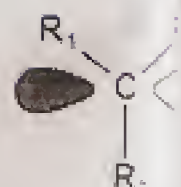
- It is because the nucleophile combines with the carbocation in the second step. Hence, the rate of an  $S_N1$  reaction does not depend on the nature of attacking nucleophile.

**(2) Stereochemical Evidence:**

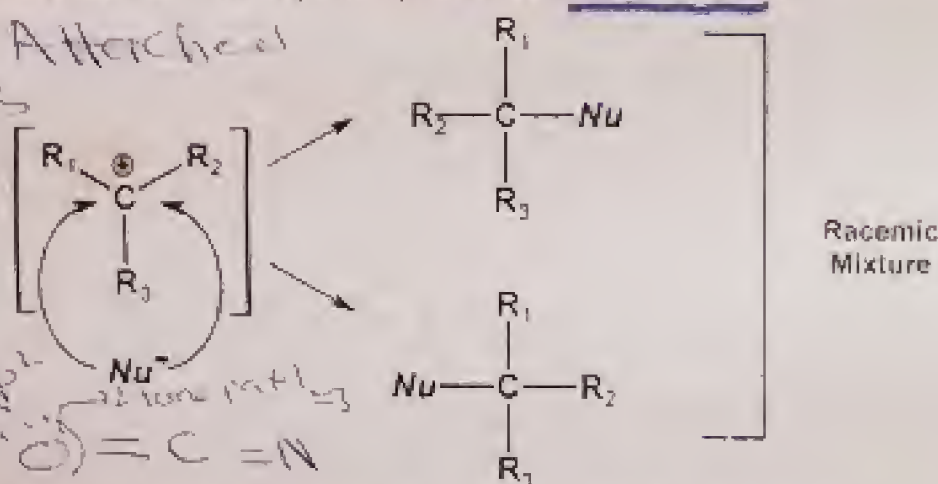
- Experiments have shown that  $S_N1$  reaction occur with partial racemization.
- The extent of partial racemization depends upon several factors including stability of carbocation.



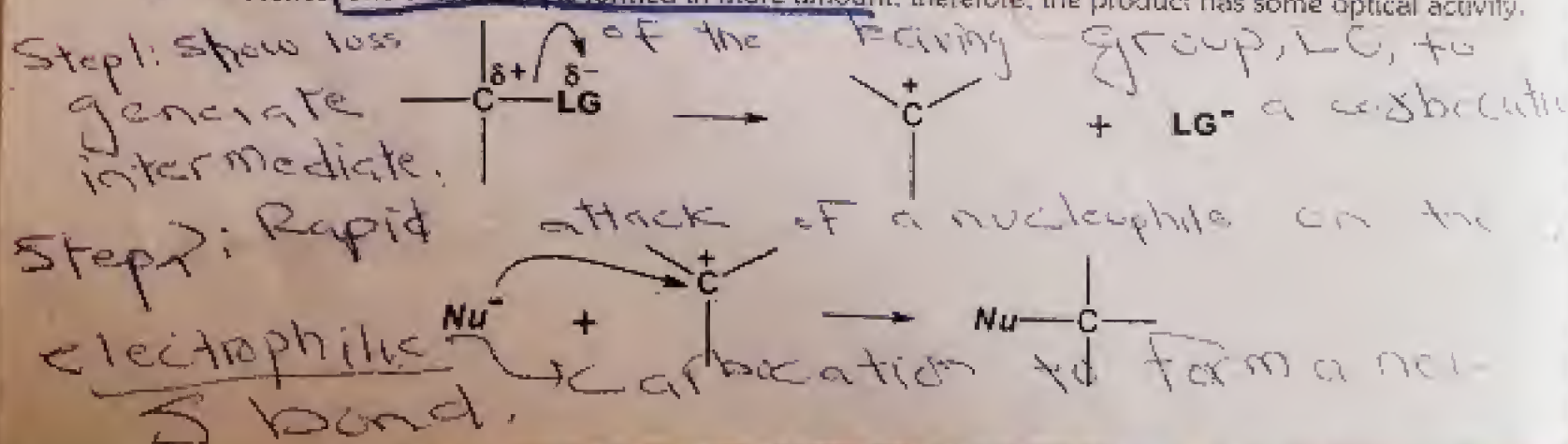
- The carbon atom of carbocation ion is  $sp^2$ -hybridized. It carries one empty p-orbital.
- The nucleophile can attach itself to the p-orbital either on the right or on the left side of carbon with equal ease. Thus expected product is a racemic mixture.



No. of Attached  
Atoms plus  
lone  
pair  
sp  
2  
sp<sup>2</sup>  
3  
sp<sup>3</sup>  
4  
sp<sup>3</sup>



- However, Partial Racemization generally occurs during  $S_N1$  reactions.
- Consider the case of unstable carbocation, the leaving group is not leaving immediately.
- Hence, the side of carbon atom to which the leaving group is attached is somewhat shielded from the attack of nucleophile.
- Thus, the attack of nucleophile is greater from the side opposite to that of leaving group leading to partial inversion of configuration.
- Hence, one enantiomer is formed in more amount, therefore, the product has some optical activity.





General Code "A" subject requires 100% attendance in theory and 80% in practical.

## S<sub>N</sub>2 MECHANISM

General: A species of nucleophilic substitution reaction.

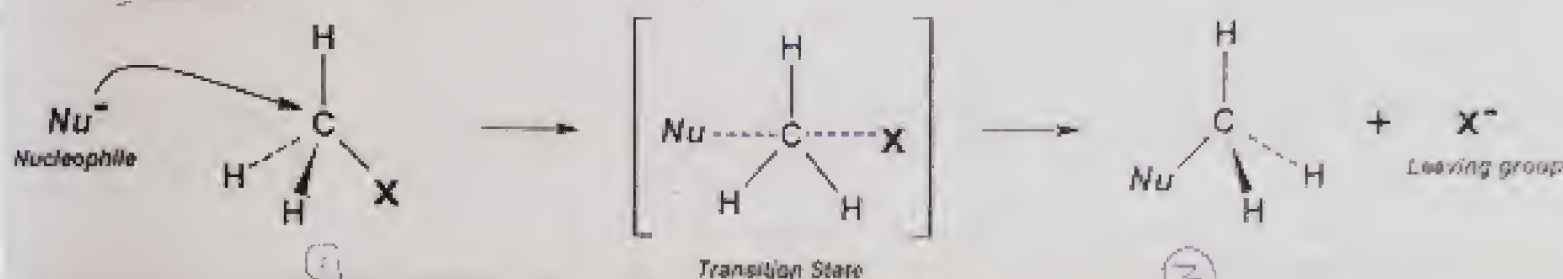
It is substitution nucleophilic bimolecular reaction. It occurs in one step.

Example



Mechanism:

- The attack of nucleophile on carbon and the departure of the halide ion take place simultaneously in single step.



- The reaction occurs in one step, so it is the rate determining step. In this one step both bond breaking and bond making processes occur simultaneously.
- Since two molecules are undergoing change in covalency in the rate determining step, therefore, it is a bimolecular nucleophilic substitution reaction.

## EVIDENCES FOR S<sub>N</sub>2 MECHANISMS

### (1) Kinetic Evidence

- The rate of an S<sub>N</sub>2 reaction depends upon the concentration of nucleophile as well as the concentration of alkyl halide.



The rate expression for the reaction can be written as

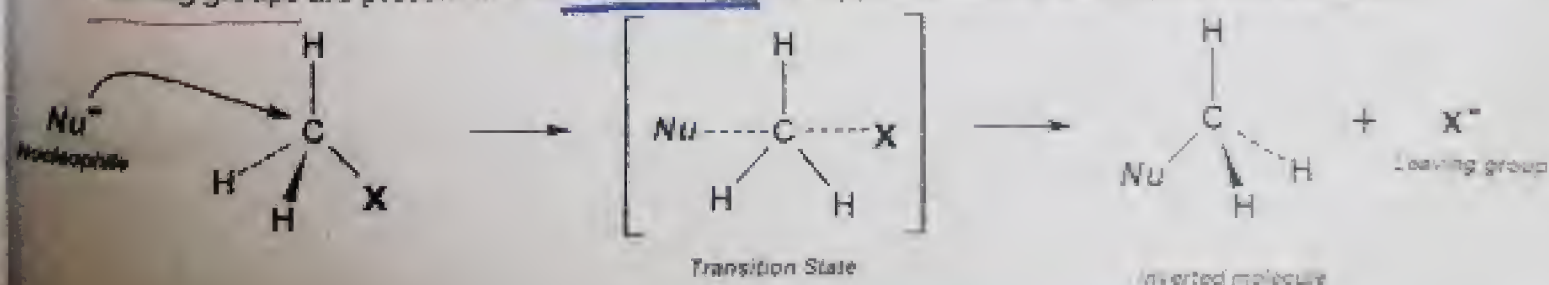
$$\text{Rate} = k[\text{Nu}][\text{R-X}] \quad \text{where } k = \text{specific rate constant.}$$



- This means that the rate of reaction will be double if the concentration of any of the two is doubled e.g., the rate of following reaction increases if conc. of either HO<sup>-</sup> or CH<sub>3</sub>-Br is increased.

### (2) Stereochemical Evidence

- A bimolecular nucleophilic substitution always occurs with inversion of configuration.
- The carbon atom in transition state is sp<sup>2</sup>-hybridized and is planar. The attacking nucleophile and the leaving groups are present in the transition state on opposite sides of electrophilic carbon atom.





COMPARISON OF  $S_N1$  AND  $S_N2$  MECHANISM

Sr. No.	$S_N1$	Sr. No.	$S_N2$
(1)	It is a two step mechanism.	(1)	It is a single step mechanism.
(2)	First step is slow one and second is fast.	(2)	It has only one step and that is slow.
(3)	It is a unimolecular reaction.	(3)	It is a bimolecular reaction.
(4)	It is favoured in polar solvents.	(4)	It is favoured in non-polar solvents.
(5)	Mostly tertiary alkyl halides give this reaction.	(5)	Mostly primary alkyl halides give this reaction.
(6)	50 % is inversion and 50% retention of configuration takes place.	(6)	100% inversion of configuration takes place.
(7)	Rate = $k [R-X]$	(7)	Rate = $k [R-X][Nu]$

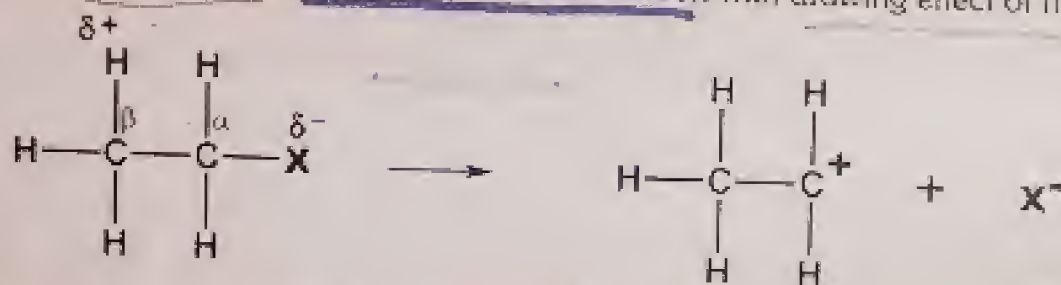
Exercise Q3 (iv) What are  $\beta$ -elimination reactions? Explain them with detail.

1,2-ELIMINATION REACTIONS ( $\beta$ -ELIMINATION REACTIONS)

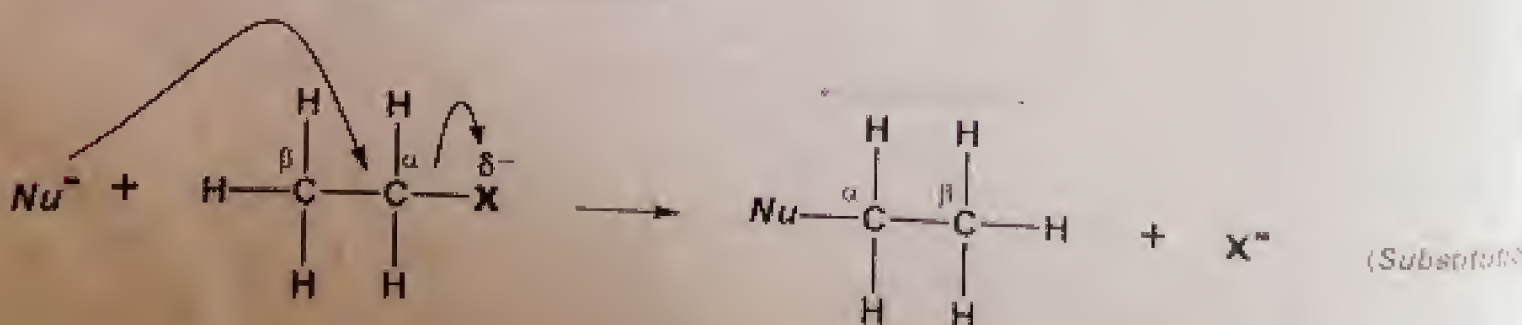
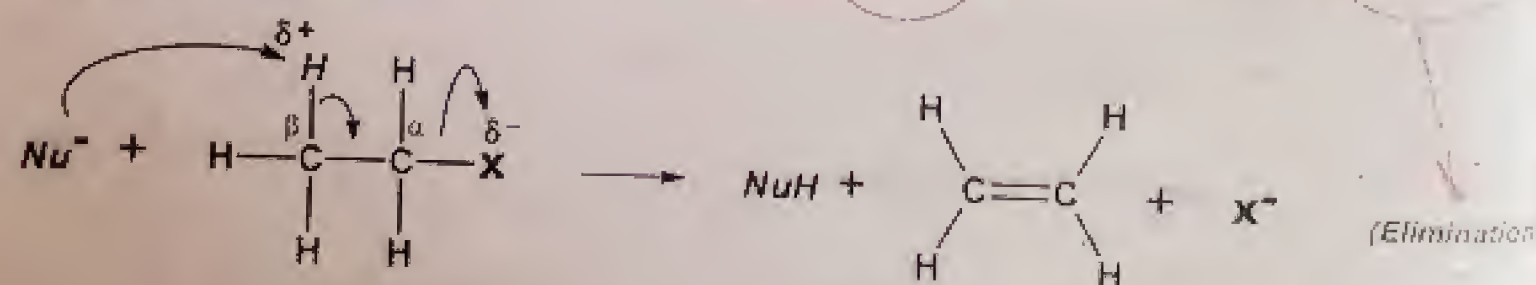
The chemical reaction in which two groups are eliminated without being replaced from a molecule is called elimination reaction. When  $\beta$ -hydrogen is eliminated, it is called  $\beta$ -elimination reaction or 1,2-elimination reaction.

Explanation:

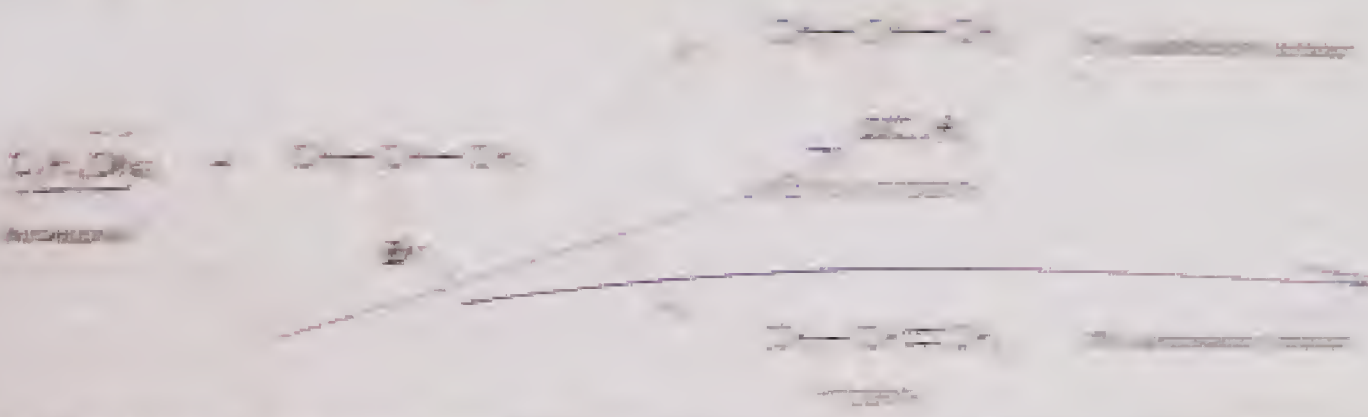
- $\beta$ -hydrogen atom in alkyl halides is slightly acidic due to electron withdrawing effect of halogen.



- The attacking nucleophile can either attack  $\alpha$ -carbon to give substitution product or  $\beta$ -hydrogen to give elimination product.







## TYPES OF ELIMINATION REACTIONS

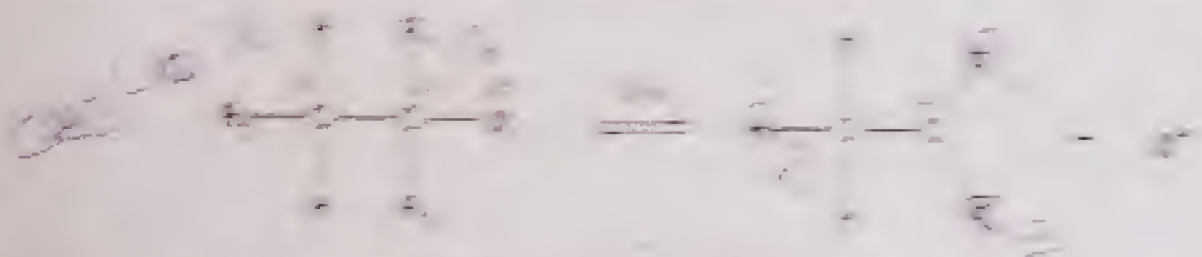
### 1. E1 MECHANISM

1. E1 mechanism involves two steps: ionization and deprotonation.

**Step-I:** Ionization

Reaction of alkyl halide with base:

Step-I: Ionization of alkyl halide to form a carbocation and a halide ion.



Step-II: Deprotonation of the carbocation by a base to form the alkene.



Since only one molecule of alkyl halide is involved in the rate-determining step, the reaction is first order and is called an **unimolecular elimination reaction**.

### EVIDENCE FOR E1 MECHANISM

#### 1. Kinetic Evidence

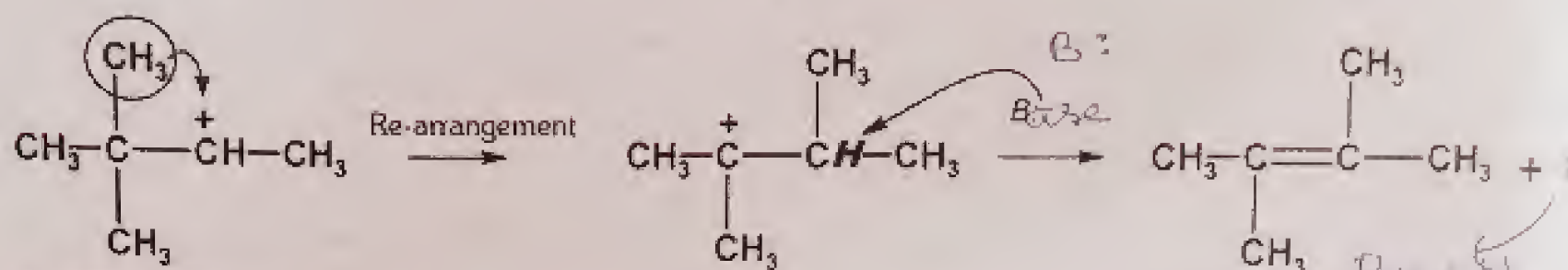
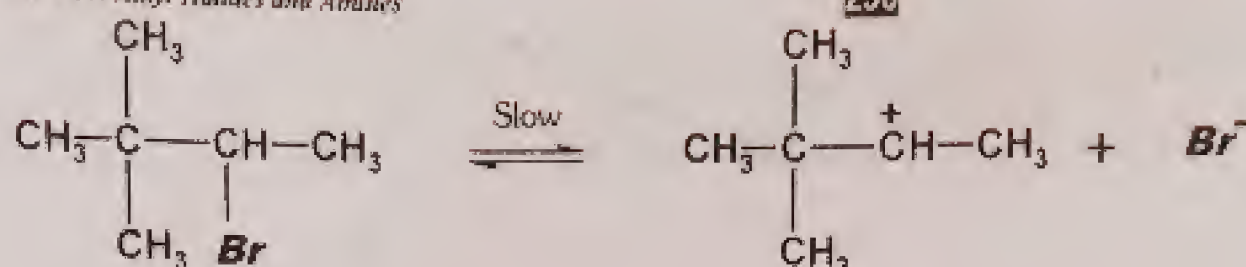
- The E1 mechanism follows first order kinetics. The rate of reaction is directly proportional to the concentration of alkyl halide.

This change in concentration of alkyl halide is observed in the reaction.

#### 2. Rearrangement of Carbocation

- The presence of carbocation as an intermediate in the E1 mechanism is confirmed by the formation of rearranged products.
- A secondary alkyl carbocation rearranges to a more stable tertiary carbocation before losing a proton.



**E2 MECHANISM**

It is bimolecular one step elimination reaction

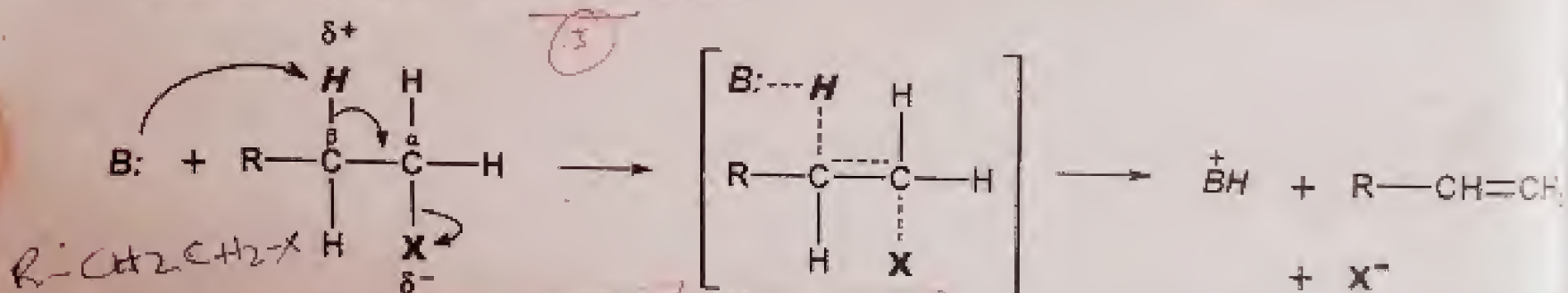
Example:

Consider the reaction,



Mechanism:

- It is a one-step reaction.
- The attacking base removes a proton from the  $\beta$ -carbon simultaneously with the formation of double bond between  $\text{C}_\alpha$  and  $\text{C}_\beta$  and the loss of halide ions.



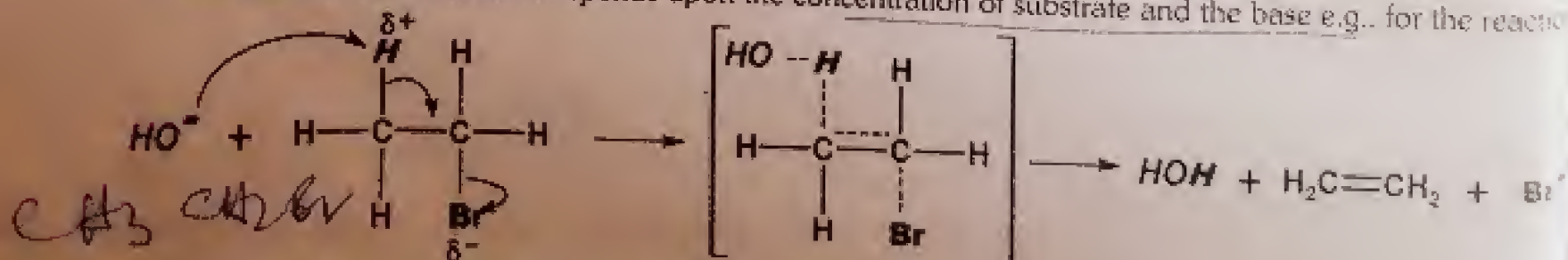
- This is rate determining step because bond breaking and bond making processes are taking place simultaneously.
- Since two molecules are undergoing a change in transition state, it is a one-step bimolecular elimination reaction.

**EVIDENCES FOR E2 MECHANISM****(1) Kinetic Evidence**

- The E2 is a one-step process in which both the substrate and the base participate. Thus, the observed law of the E2-reaction is

$$\text{Rate} = k [\text{Substrate}][\text{Base}]$$

Thus, the rate of E2-reaction depends upon the concentration of substrate and the base e.g., for the reaction



The rate of reaction follows second order kinetics i.e.,  $\text{Rate} = k[\text{CH}_3\text{CH}_2\text{Br}][\text{HO}^-]$



## SUBSTITUTION VERSUS ELIMINATION REACTIONS

- The substitution and elimination reaction gives different products. However, there is always a competition between them because of close similarity in their mechanism.
- Energetically substitution is more favorable, therefore, it is the dominant reaction in the substitution-elimination competition. It is because more bonds are to be broken in elimination reactions.
- Elimination occurs only in the presence of beta hydrogen ( $\beta$ -H). However, substitution reactions do not require this condition.

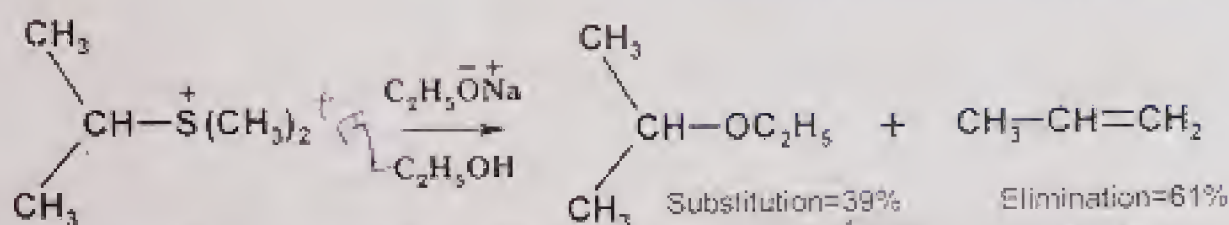
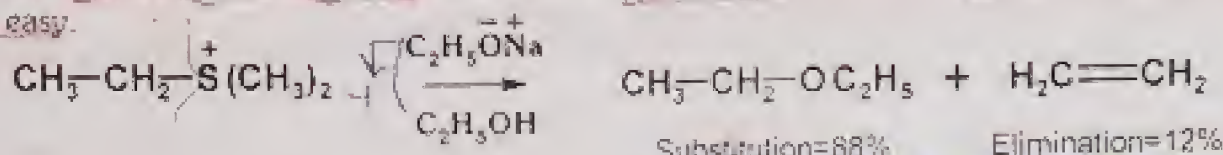
Following factors help to compare these two path ways:

### (i) Structure of Substrate:

Crowding within the substrate favors elimination over substitution.

It is because the approach of the nucleophile to  $\alpha$ -carbon is difficult for substitution.

However, the elimination is favorable because the removal of  $\beta$ -H atom by base from tertiary planar carbocation is easy.

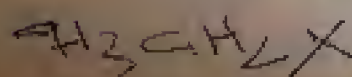
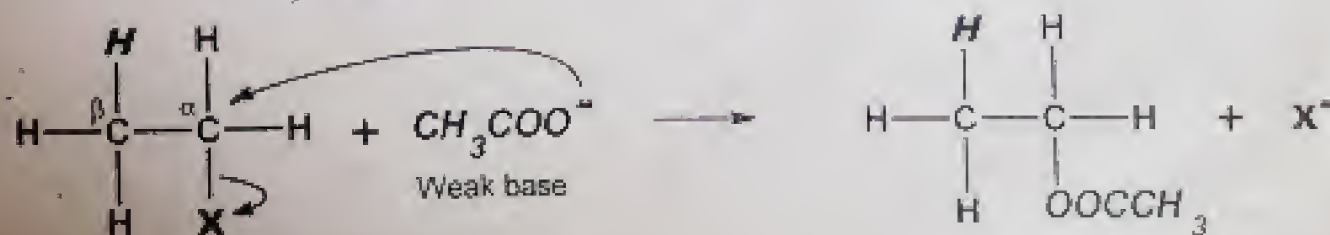
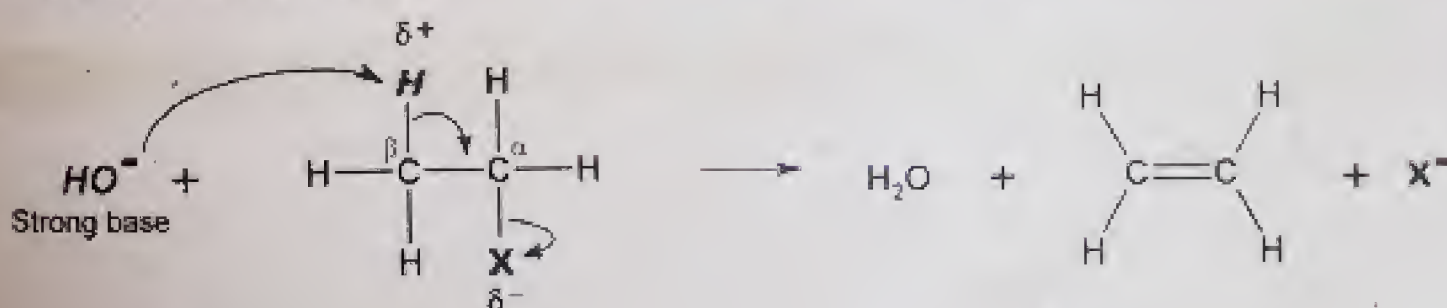


**Remember!**  $-\text{S}^+(\text{CH}_3)_2$  group is removed as shown below. It is not shown in the above reaction.



### (ii) Nature of Base:

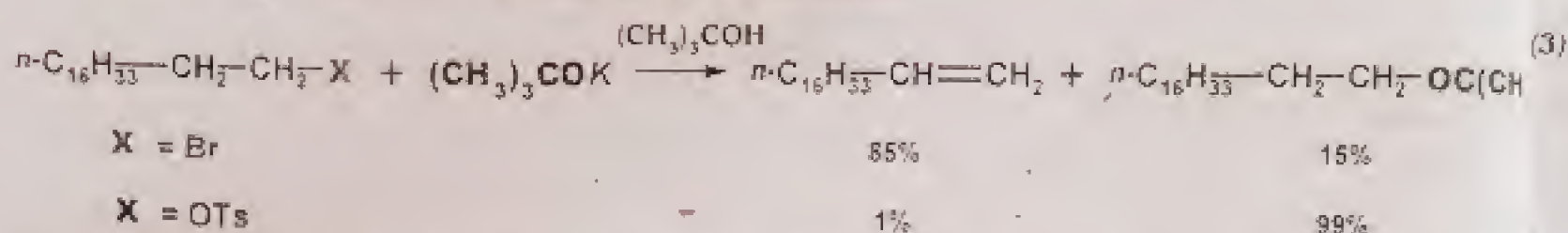
- When the electron pair donor is a strong base, e.g.,  $\text{HO}^-$ ,  $\text{RO}^-$  etc., the dominant reaction is E2. The  $\text{S}_\text{N}2$  reaction is a side reaction.
- However, when the nucleophile is a weak base like  $\text{X}^-$ ,  $\text{RS}^-$ , etc., the main reaction will be  $\text{S}_\text{N}2$ . The E2 will be a minor side reaction.





**(iii) The nature of Leaving Group:**

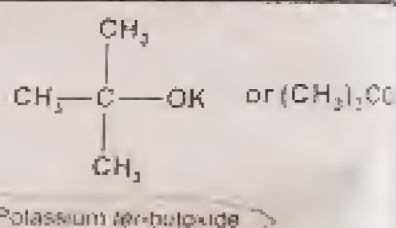
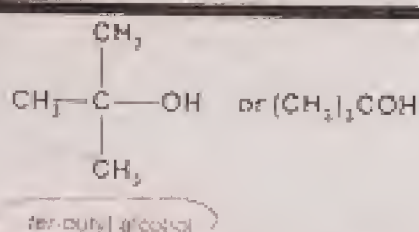
- The role of leaving groups in Elimination reactions is similar to that in substitution reactions.
- In unimolecular reactions ( $E1$  and  $S_N1$ ), it does not affect the mechanism. It is because leaving group is left in the first step. While the elimination and substitution products decided in the second step with carbocation.
- However, in the bimolecular reactions the nature of product greatly depends upon the nature of leaving group, e.g. consider the following bimolecular reaction,



Generally a good leaving group favours substitution reaction more than elimination reaction

**Remember:**

OTs = Tosylate group  
(See page 230)

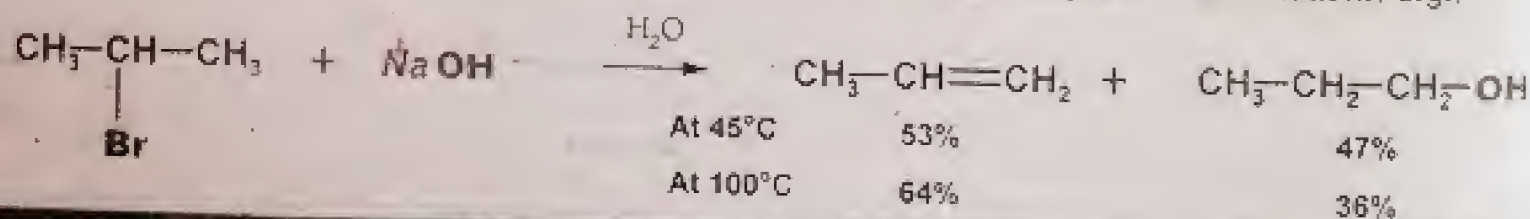
**(iv) Nature of Solvent**

- Elimination is favored more than substitution by decreasing the solvent polarity. Thus, alcoholic KOH affects elimination while more polar aqueous KOH is used for substitution.
- $E1$  is favored by polar solvents like  $S_N1$  reaction.
- In non-polar solvents, the reaction will follow  $E2$ -mechanism.

**(v) Effect of Temperature**

An increase in temperature will favor more than substitution.

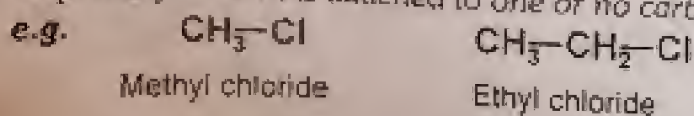
It is because substitution reaction involve less reshuffling of bonds as compared to eliminations, e.g.,

**QUICK QUIZ (1)****(1) What are monohaloalkanes**

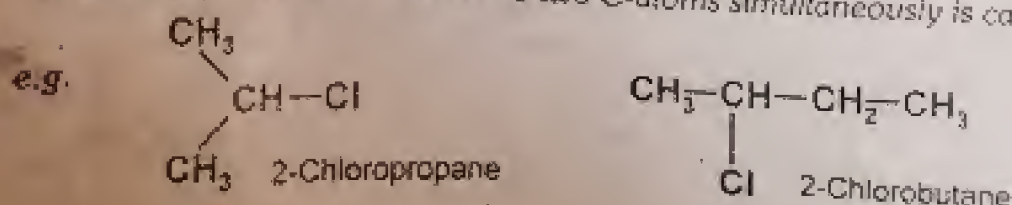
Monohaloalkanes are called alkyl halides. These have general formula  $\text{R-X}$ . These may be classified as primary, secondary or tertiary alkyl halides.

**(2) What are primary, secondary and tertiary carbons atoms**

- A primary C-atom is attached to one or no carbon atom is called a primary C-atom.

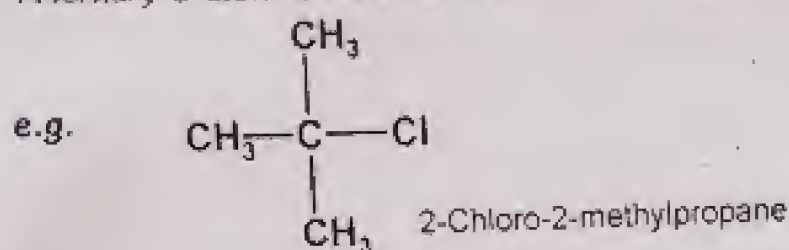


- A Secondary C-atom is attached to two C-atoms simultaneously is called a secondary C-atom.



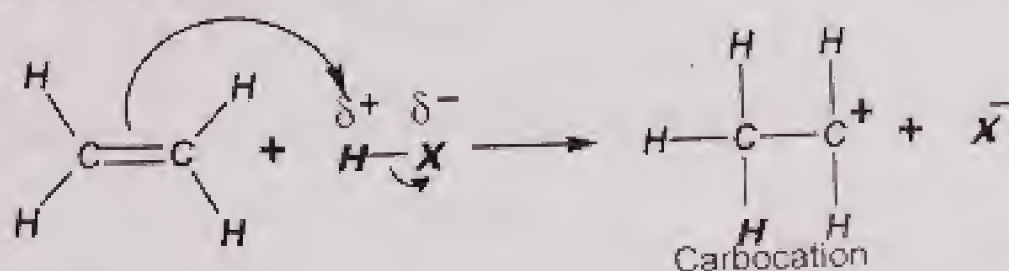


- A tertiary C-atom is attached to three C-atoms simultaneously is called a tertiary C-atom.



### 3) What is carbonium ion

A carbocation is a reaction intermediate. It is trivalent with a positive charge on carbon atom. It can be produced as follows



**NOTE:** Carbonium ion is an old term. It is no longer in use. The current term for such species is carbocation.

### (4) What is leaving group

Leaving group is a nucleophile that leaves during substitution reaction with an unshared pair of electrons.

- The incoming nucleophile must be stronger than the leaving group.
- Good Leaving Groups are:  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{HSO}_4^-$
- Poor leaving groups are  $\text{OH}^-$ ,  $\text{OR}^-$  and  $\text{NH}_2^-$ .
- Iodide ion is a good nucleophile as well as a good leaving group.

### (5) What is $sp^3$ -hybridization

The process of mixing one s orbital and three p orbitals to form four new equivalent  $sp^3$  hybrid orbitals is called  $sp^3$  hybridization.

The ratio of s and p character in each  $sp^3$  hybrid orbitals is 1:3. Thus, each  $sp^3$ -hybrid orbital has 25% s-character and 75% p-character.

e.g. In  $\text{CH}_4$ , carbon atom undergoes  $sp^3$  hybridization.

### (6) Define bond polarity

The property of shared pair of electrons being closer to one atom than the other in a covalent bond is called bond polarity

e.g. the bond between H and Cl in HCl is a polar bond.

### (7) Define bond energy

The amount of energy required to break one mole of similar bonds in a molecule is called bond energy

e.g.  $\text{H}_2 \rightarrow 2\text{H}$   $\Delta H = 435 \text{ kJ/mol}$ . Thus, bond energy of H-H bond is 435 kJ/mol

### (8) What is a nucleophile?

A Species in search of positive charge is called a nucleophile.

Or It is species rich in electron and has an unshared pair of electrons available for bonding

It may be negatively charged or neutral

#### Examples

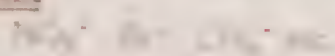
$\text{HO}^-$	Hydroxide ion	$\text{NH}_3$	Ammonia
$\text{C}_2\text{H}_5\text{O}^-$	Ethoxide ion	$\text{H}_2\text{O}$	Water



(9) What is an electrophile?

Species in search of negative charge is called an electrophile.

Examples



(10) Define inductive effect.

The polarisation of a bond caused by an adjacent more bond is known as the Inductive Effect.

(11) Define resonance effect.

The decrease in electron density by the presence of a double bond with corresponding increase in electron density at some other position is called Resonance Effect or Mesomeric Effect.

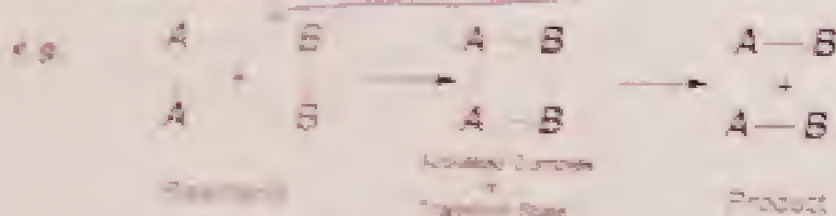
(12) What is racemisation?

The process in which an optically active compound is converted into a racemic mixture is called racemisation.

(13) Define transition state?

The highest energy species formed between reactants and products during a chemical reaction is called a transition state.

It is also called activated complex.



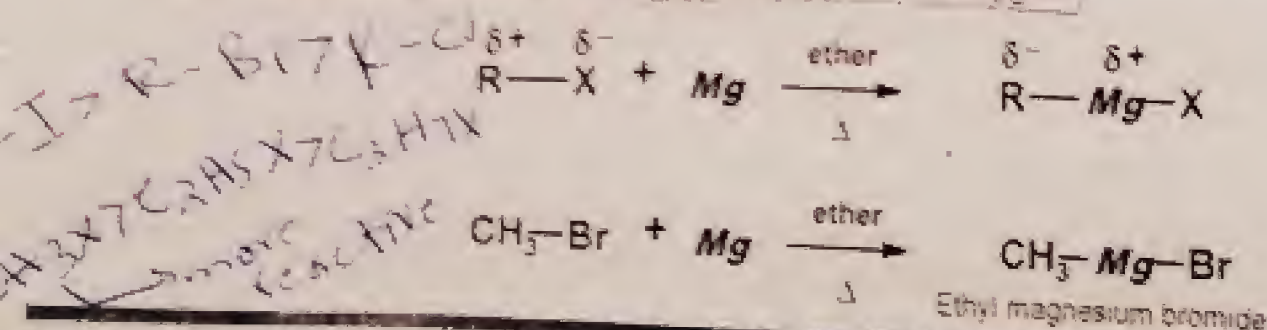
## ORGANOMETALLIC COMPOUNDS (GRIGNARD'S REAGENTS)

Exercise Q3 and Discuss the preparation and reactivity of Grignard's reagent.

### Preparation of Grignard's Reagents

Procedure

- Magnesium metal cut into small pieces is added to a solution of an alkyl halide or aryl halide in or dry ether.
- The reaction mixture is heated with electric heater in a round bottom flask fitted with condenser and other arrangement to avoid the contact of moisture or oxygen.



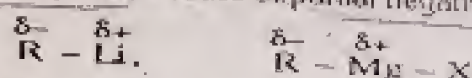
Important

- Alkyl bromides are generally used in the preparation Grignard's reagents because of its intermediate reactivity.
- When more reactive alkyl halides are used, the high boiling solvent such as tetrahydrofuran is employed. It because reflux.
- When less reactive aryl halides are used.
- Alkyl magnesium halides are not isolated but are used as ethereal layers.

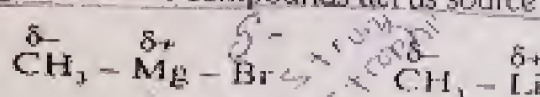


# REACTIVITY

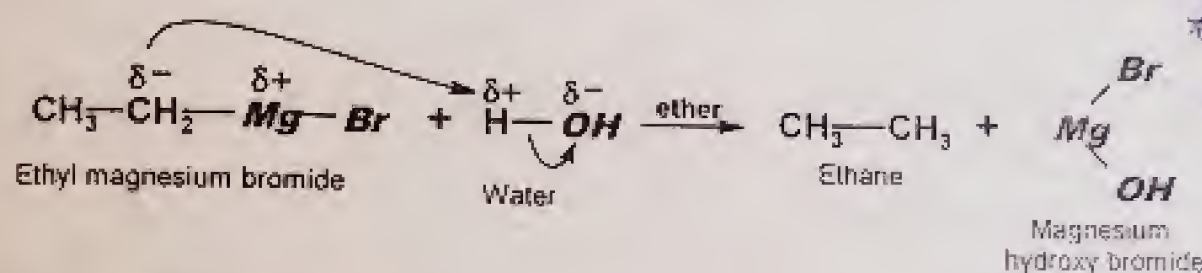
- Organometallic compounds are nucleophile because of partial negative charge on the carbon of alkyl group



- Carbon atom being more electronegative than metals such as Mg, Li etc., the alkyl group as a whole bears partial negative charge. Thus, organometallic compounds act as source of nucleophile.



- The following reaction supports the nucleophilic character of organic metallic compounds.



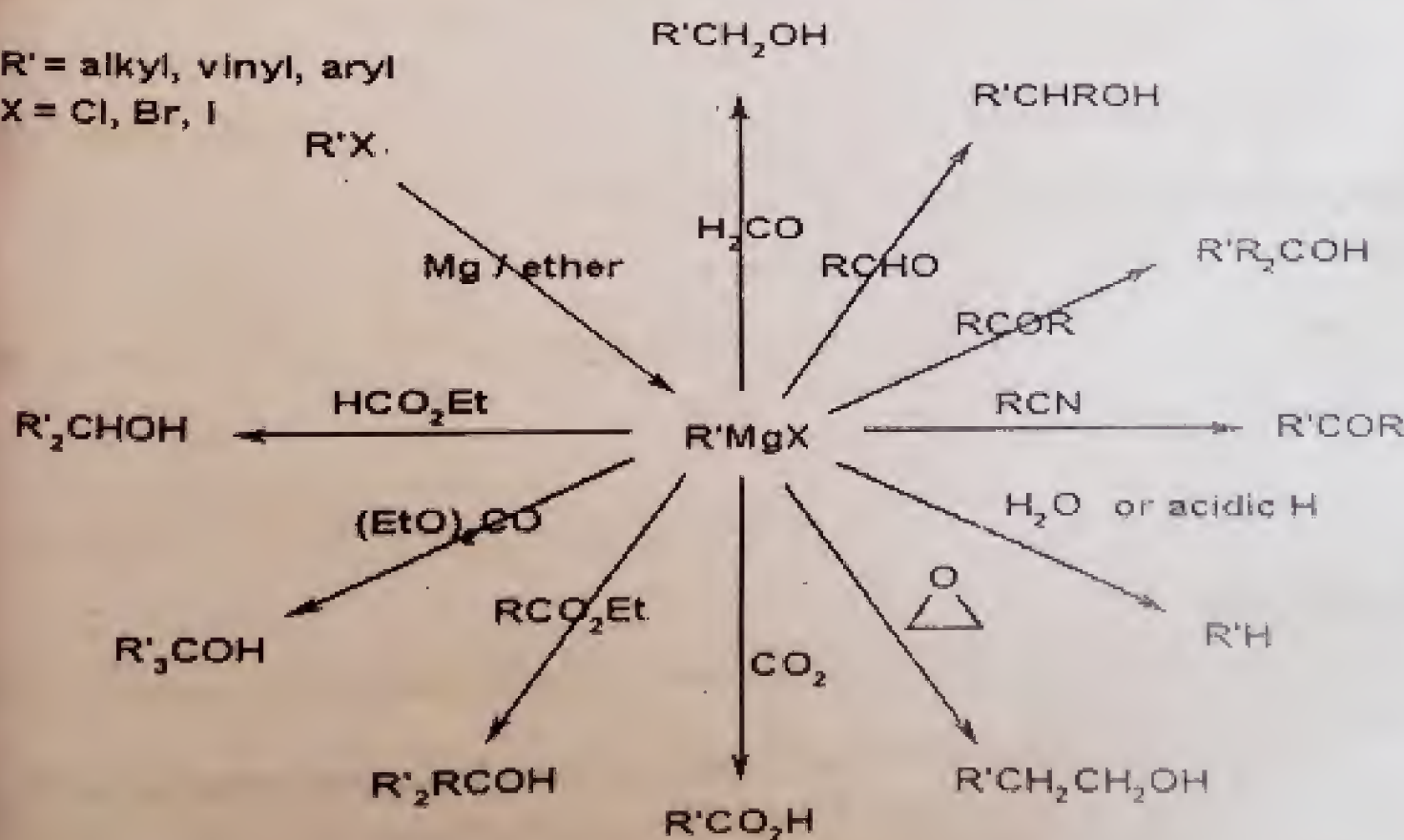
\*Most Reaction used in organic synthesis

**Remember!** Abbreviations for common Alkyl/Aryl groups. These are to be used in next reactions. Methyl (Me), Ethyl (Et), n-Propyl (n-Pr), isopropyl (iso-Pr), Phenyl (Ph) etc.

## REACTIONS OF GRIGNARD'S REAGENTS

### Brief Summary

R' = alkyl, vinyl, aryl  
X = Cl, Br, I



Typical work-up for these reactions:

1. Dilute aqueous acid or
2. Aqueous ammonium chloride



## (1) With Aldehydes and Ketones

This is done to produce primary, secondary and tertiary alcohols.

These reactions are carried in the presence of ether followed by acidic hydrolysis (i.e.  $\text{H}_3\text{O}^+$ ).

### Classification of Monohydric Alcohols

The alcohols containing only one hydroxyl group (OH) are called monohydric alcohols.

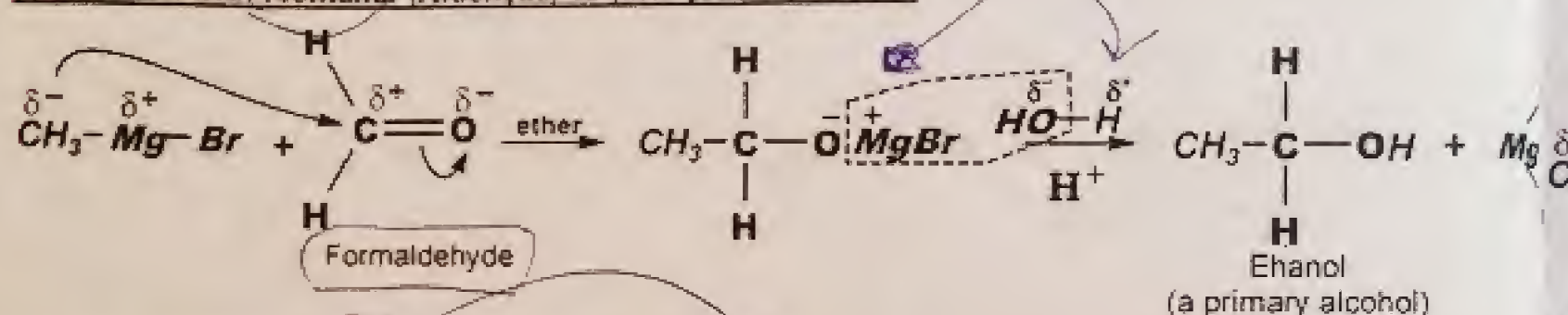
Monohydric alcohols are classified into the three types.

(i) Primary alcohols

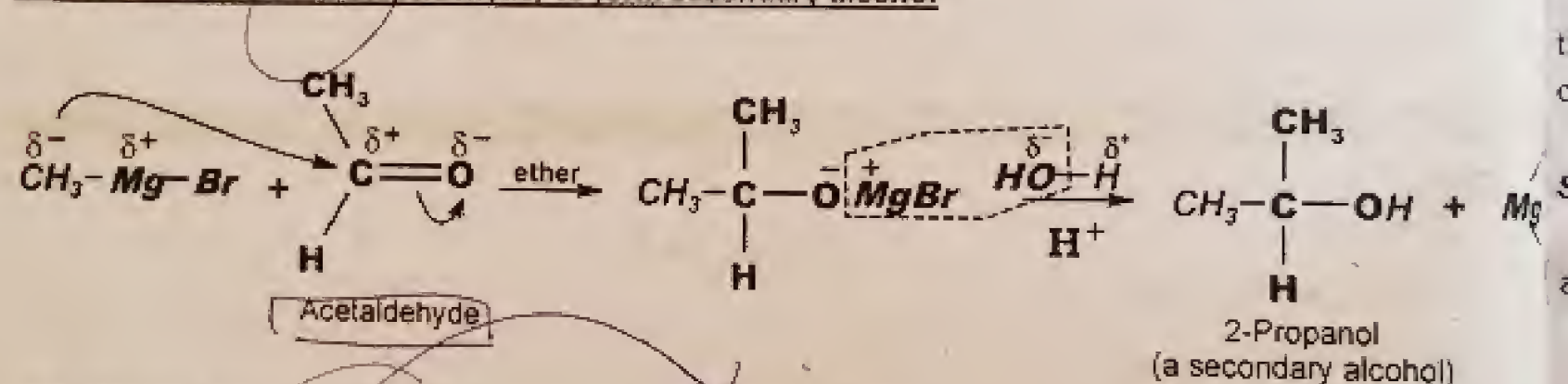
(ii) Secondary alcohols

(iii) Tertiary alcohols

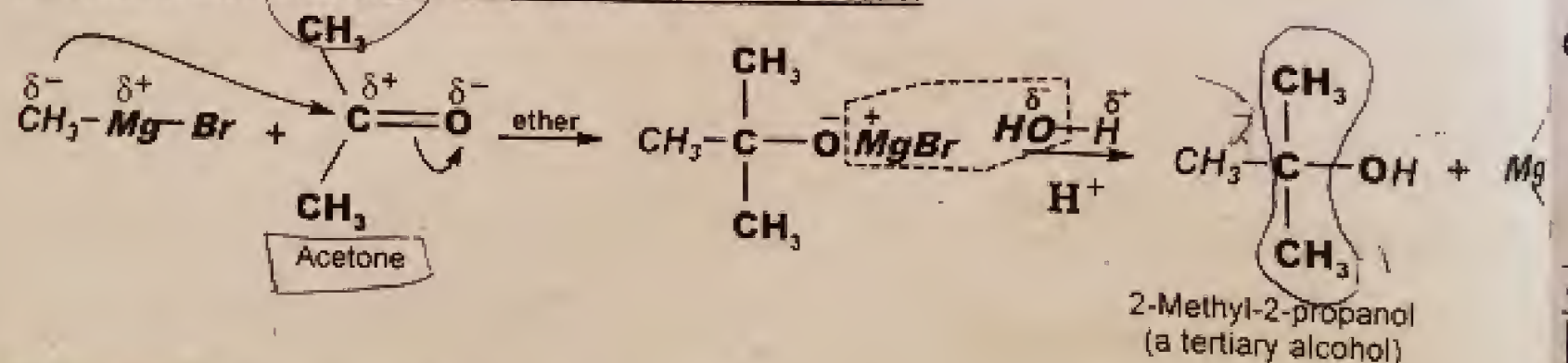
### (i) Reaction with Methanal (Aldehyde) to form primary alcohol



### (ii) Reaction with Ethanal (Aldehyde) to form secondary alcohol



### (iii) Reaction with Propanone (Ketone) to form tertiary alcohol



## (2) With Esters

- Carboxylic esters,  $\text{R}_1\text{COOR}_2$ , react with 2 equivalents of organolithium or Grignard reagents to give tertiary alcohols.
- The tertiary alcohol contains 2 identical alkyl groups which comes from two units of Grignard reagent.
- The reaction proceeds via a ketone intermediate. It further reacts with the second equivalent of organometallic reagent to give tertiary alcohol.
- Since the ketone is more reactive than the ester, the reaction cannot be stopped at the ketone stage. Hence this reaction cannot be used for the preparation of ketones.



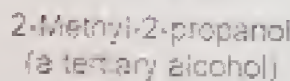
The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar carbonyl group of the ester. Electrons from the C=O move to the electronegative O creating an intermediate metal alkoxide complex.

The tetrahedral intermediate collapses and displaces the alcohol portion of the ester as a leaving group. This produces a ketone as an intermediate.



The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar carbonyl group of the ketone. Electrons from the C=O move to the electronegative O creating an intermediate metal alkoxide complex.

This is the work-up step. It is a simple acid/base reaction. Protonation of the alkoxide oxygen creates the alcohol product from the intermediate complex.

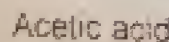


(3) With  $\text{CO}_2$  (Carbonation of Grignard Reagents,  $\text{RMgX}$ )

The nucleophilic C in the Grignard reagent adds to the electrophilic C in the polar carbonyl group, electrons from the C=O move to the electronegative O creating an intermediate magnesium carboxylate complex.

**Step 2:**

This is the work-up step. It is a simple acid/base reaction. Protonation of the carboxylate oxygen creates the carboxylic acid product from the intermediate complex.





## QUICK QUIZ-2

### (1) What are Organometallic Compounds?

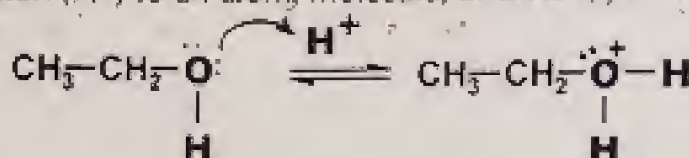
The compounds containing at least one bond between carbon atom of organic compound and a metal atom are called organometallic compounds.

Examples: Grignard's reagent, e.g.  $\text{H}_3\text{C}-\text{Mg}-\text{Cl}$ ; Alkyl Lithium compounds, e.g.  $\text{H}_3\text{C}-\text{Li}$

### (2) Define protonation

The addition of a proton ( $\text{H}^+$ ) to an atom, molecule, or an ion, forming its conjugate acid is called protonation.

Example:



### (3) What is formula of Organolithium?

The general formula of organolithium compounds is  $\text{R}-\text{Li}$ , where  $\text{R}$  is an alkyl group or  $\text{Ar}-\text{Li}$ , where  $\text{Ar}$  is an aromatic group.

Examples: Methyl lithium,  $\text{H}_3\text{C}-\text{Li}$ ; Phenyl lithium,  $\text{Ph}-\text{Li}$

### (4) How does $\text{R}-\text{Mg}-\text{X}$ reacts with $\text{CO}_2$

Solved on Page 232 above

### (5) Write the formula of Grignard's reagent.

The general formula of Grignard's reagent is  $\text{R}-\text{Mg}-\text{X}$ , where  $\text{R}$  is an alkyl group and  $\text{X}$  is a halogen atom.

Examples: Methyl magnesium chloride,  $\text{H}_3\text{C}-\text{Mg}-\text{Cl}$ ; Ethyl magnesium bromide,  $\text{H}_3\text{C}-\text{CH}_2-\text{Mg}-\text{Br}$

## AMINES

Exercise Q3 (vi) What are the amines? Give its nomenclature.

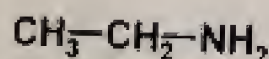
The organic compounds containing  $\text{NH}_2$  functional groups are called amines.

### NOMENCLATURE

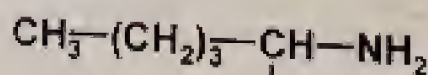
#### 1. Common System of Naming

##### Aliphatic Amines

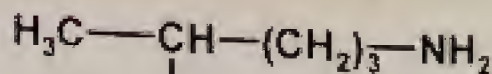
The common names of amines are written by adding the suffix-amine to the name of alkyl or aryl radicals.



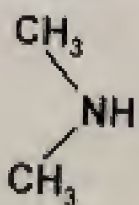
Ethyl amine



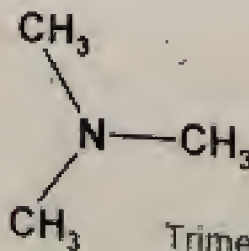
sec-Hexyl amine



Isohexyl amine



Dimethyl amine  
(a secondary amine)

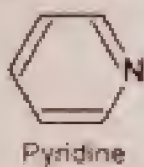


Trimethyl amine  
(a tertiary amine)

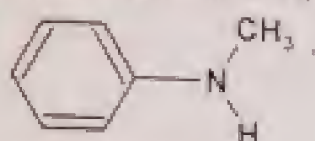


### Aromatic Amines

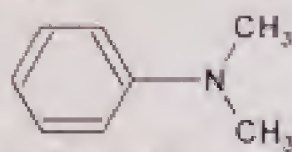
Aniline,  $C_6H_5NH_2$  containing methyl group on the ring is called Toluidine. If there is some alkyl group substituted in  $-NH_2$  its name is represented by writing N-(alkyl group). It indicates that alkyl group is located on N-atom and not on the ring. If there are two substituent on N, it is repeated twice.



Pyridine



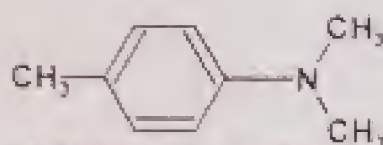
N-Methylaniline



N,N-dimethylaniline



p-Toluidine

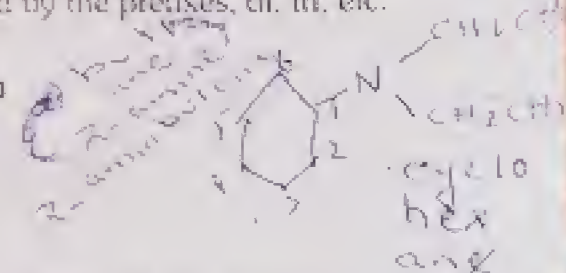
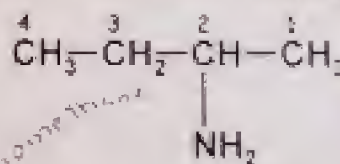
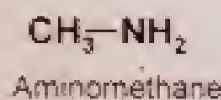
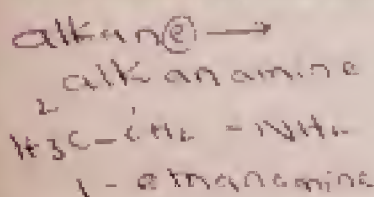


N,N-Dimethyl-p-toluidine

### 2. IUPAC System of Naming Amines

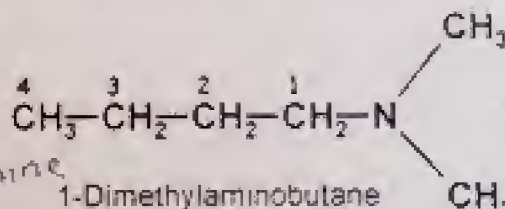
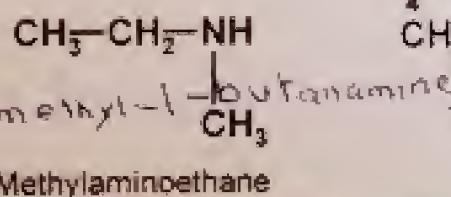
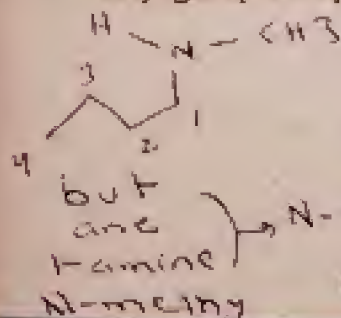
#### Primary amines

- Select the longest continuous carbon chain to which amino group is attached
- The amino group is indicated by a prefix-amino followed by name of hydrocarbons.
- Number the carbon atoms in such a way so that substituent gets smallest possible number
- The position of amino group is indicated by a number obtained by numbering the chain of hydrocarbon.
- If more than one amino groups are present, then their number is indicated by the prefixes, di, tri, etc.



#### Secondary and Tertiary amines

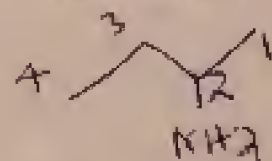
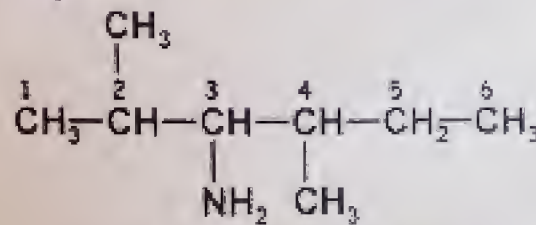
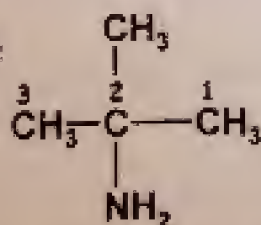
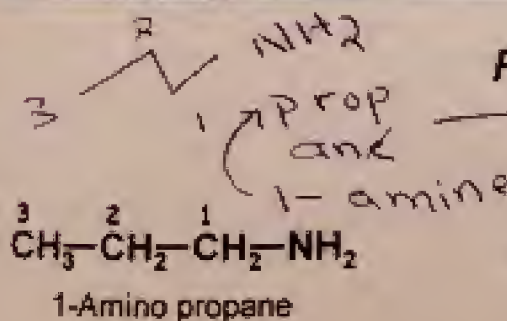
- Secondary and tertiary amines are named by using a compound prefix that includes the names of all alkyl group except the largest alkyl group (e.g. dimethylamino, methylethylamino etc.)



N,N-diethylcyclohexylamine

### More Practice

#### Primary amines

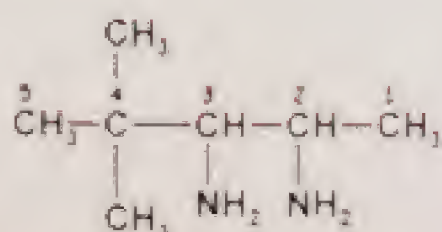


butane  
 2-amine

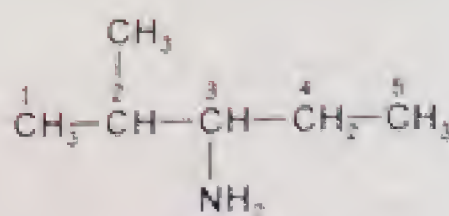
2-butanamine  
 1° amine

because amino group is attached to one carbon



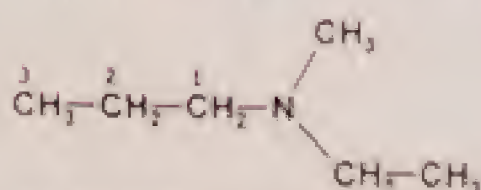


2,3-Diamino-4,4-dimethylpentane

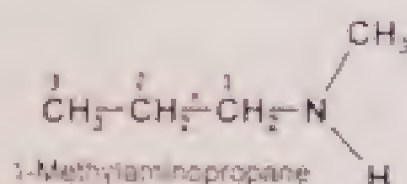


3-amino-2-methylpentane

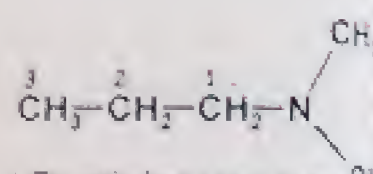
### Secondary and Tertiary amines



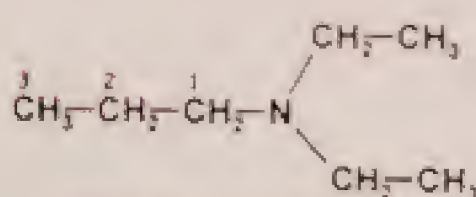
1-Methylethylaminopropane



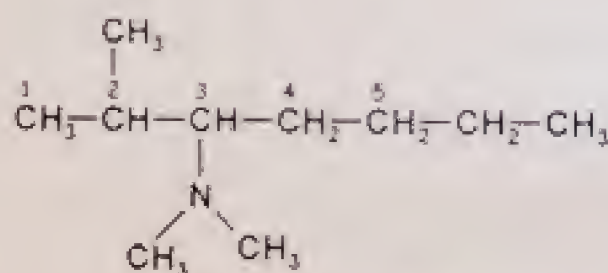
1-Methylaminopropane



1-Dimethylaminopropane



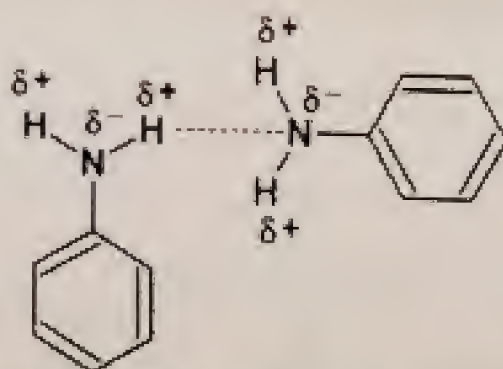
1-Diethylaminopropane



3-dimethylamino-2-methylheptane

### PHYSICAL PROPERTIES:

- The polar nature of the N-H bond (due to the electronegativity difference of the two atoms) results in the formation of hydrogen bonds with other amine molecules or other H-bonding systems (e.g. water).
- Thus, amines have
  - high melting and boiling points compared to analogous alkanes
  - high solubility in aqueous media

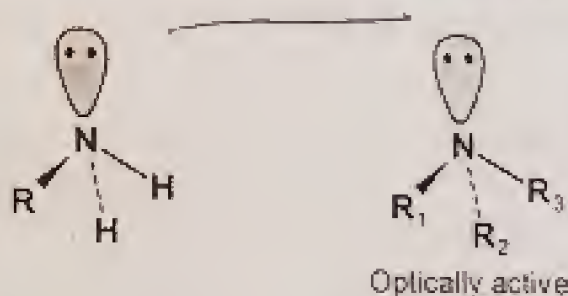


Intermolecular hydrogen bonding in amines



### STRUCTURE:

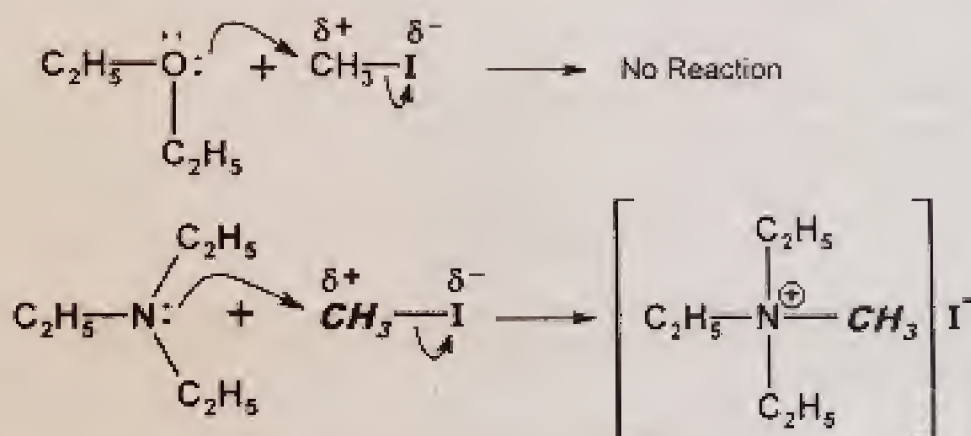
- In amines, nitrogen atom is  $sp^3$ -hybridized and has nearly tetrahedral structure.
- It forms three sigma bonds with its three  $sp^3$ -hybrid orbitals while the fourth non-bonding  $sp^3$ -hybrid carries a pair electron.



- The non-bonding electron pair is extremely important in explaining the chemical behavior of amines. It is because it is responsible for the basic and nucleophilic properties of these compounds.
- An amine with three different groups is optically active.

### BASICITY:

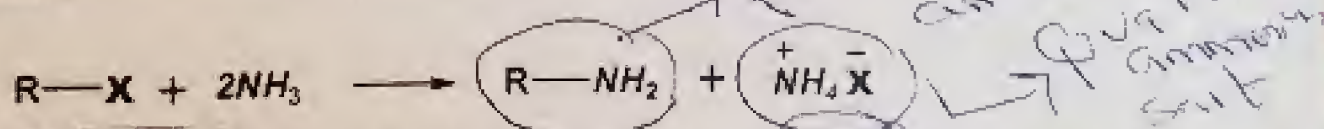
- Amines may act as bases towards acids and as Nucleophiles towards electrophile.
- They are more basic than alcohols and ethers and they are also more nucleophilic.  
e.g., ether does not react whereas at the same temperature amines gives addition product with  $CH_3-I$ .



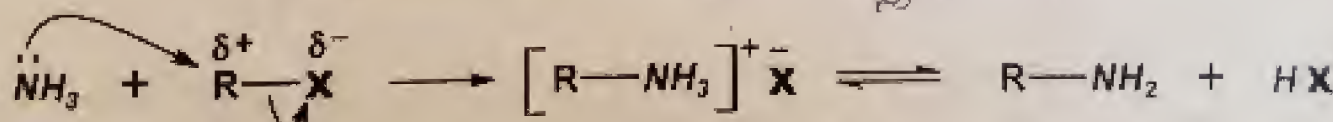
## PREPARATION OF AMINES

### (I) ALKYLATION OF AMMONIA BY ALKYL HALIDES

- The general reaction is

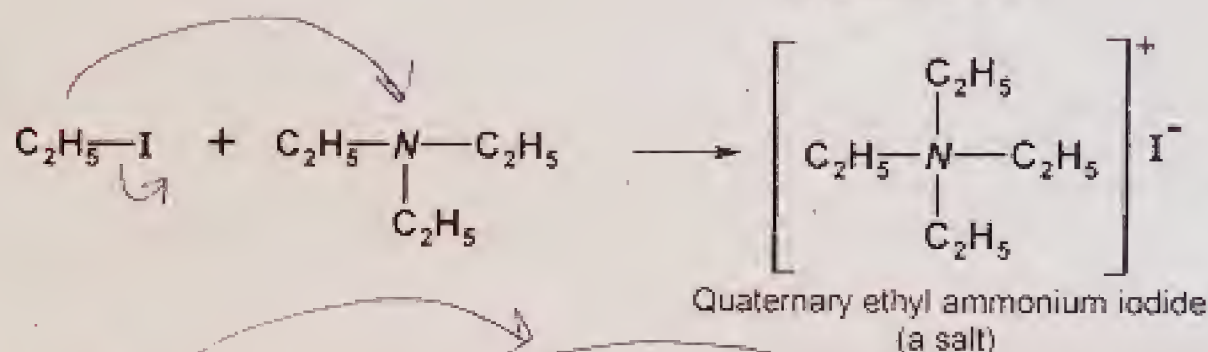
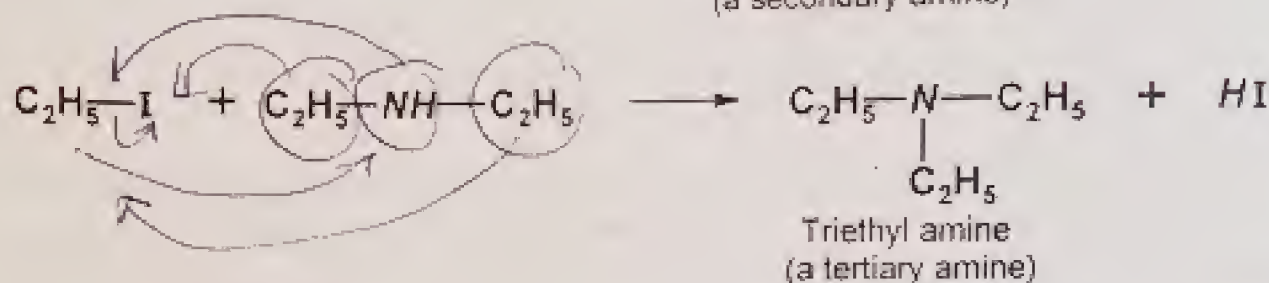
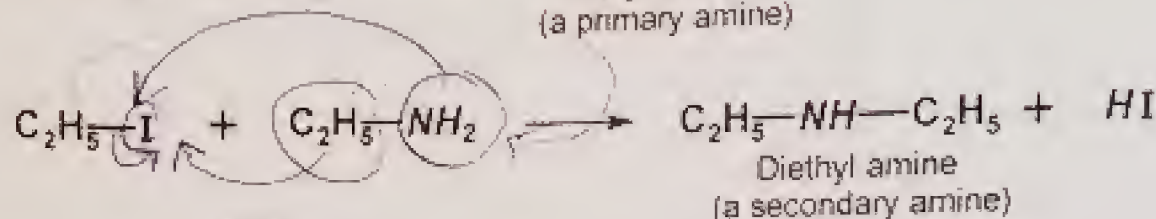


- When an alcoholic or aqueous solution of ammonia is heated with an alkyl halide, a mixture of prim-, sec-, ter- amines and a quaternary ammonium salt is obtained.
- The reaction occurs with nucleophilic displacement of halide by ammonia or amines.





- This reaction is further alkylation, e.g., accompanies by the following reactions

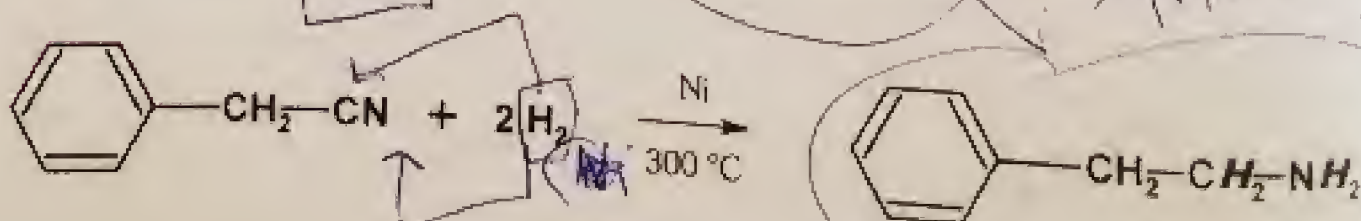
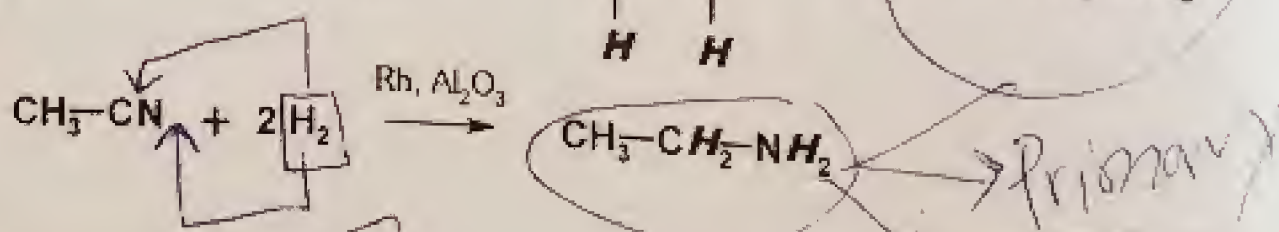
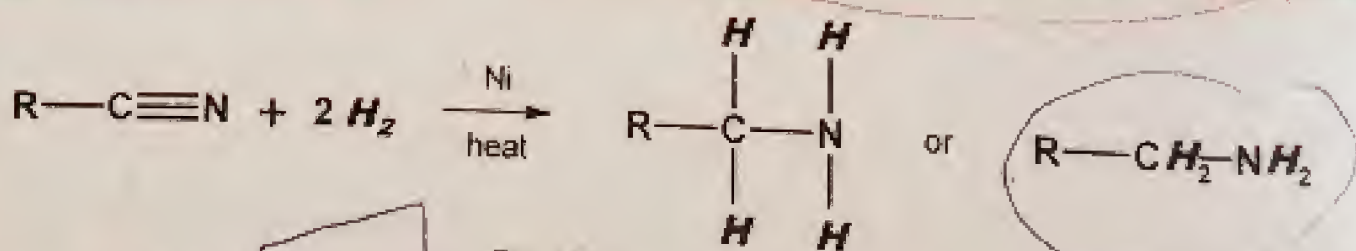


- At the end of the reaction, addition of strong alkali such as KOH liberates free amines from their salts; the quaternary salt is unaffected.
- The three amines are separated by fractional distillation.
- Over alkylation can be avoided by using excess of ammonia but the yield is low.

## (2) REDUCTIONS OF NITROGEN CONTAINING FUNCTIONAL GROUPS:

### (i) REDUCTION OF NITRILES

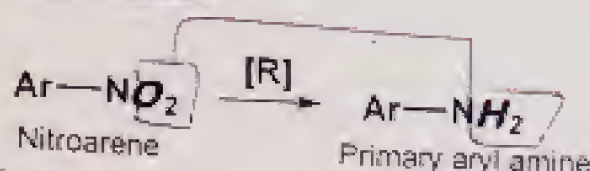
- Reduction of alkyl or aryl nitriles gives primary amines.
- The reduction may be brought about by  $\text{LiAlH}_4$ , or sodium in ethanol.
- Catalytic hydrogenation with  $\text{Rh-Al}_2\text{O}_3$ , Pt or Raney nickel may also be employed to get primary amines.



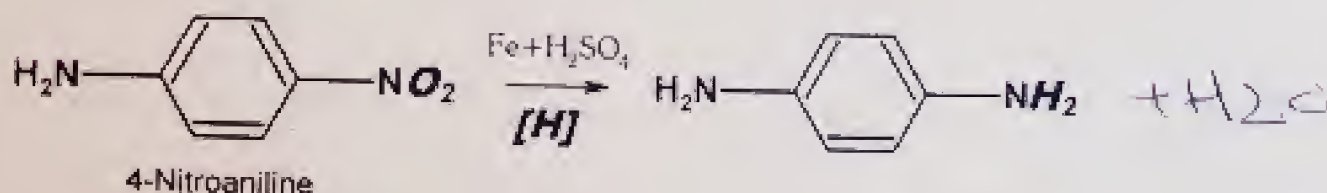
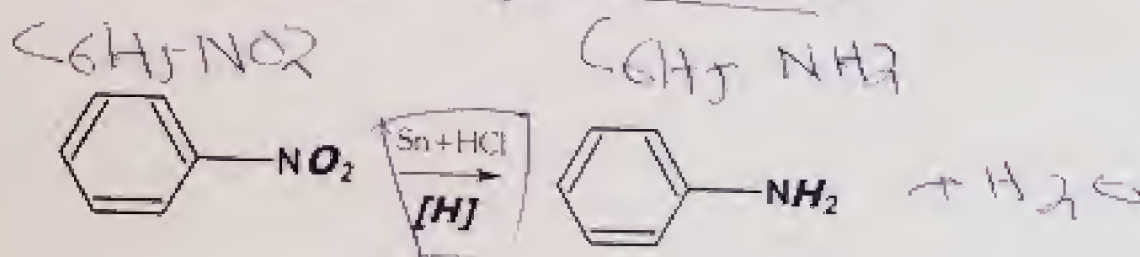


## (ii) REDUCTION OF NITRO COMPOUNDS

- The general reaction is

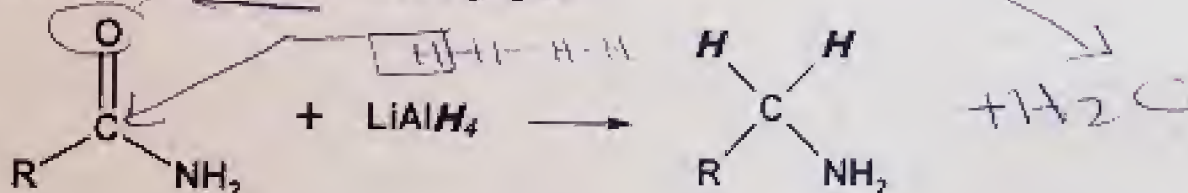


- Nitroarenes can be reduced to primary aryl amines.
- Typical reducing agents include,  $\text{Fe} / \text{H}^+$ ,  $\text{Sn} / \text{H}^+$  or catalytic hydrogenation (e.g.  $\text{H}_2 / \text{Pd}$ )
- Nitro compounds on catalytic or chemical reduction produce primary amines.

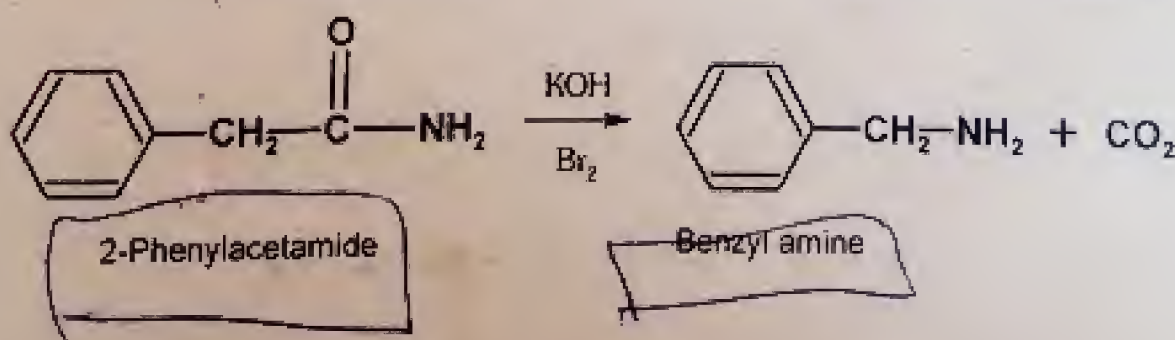
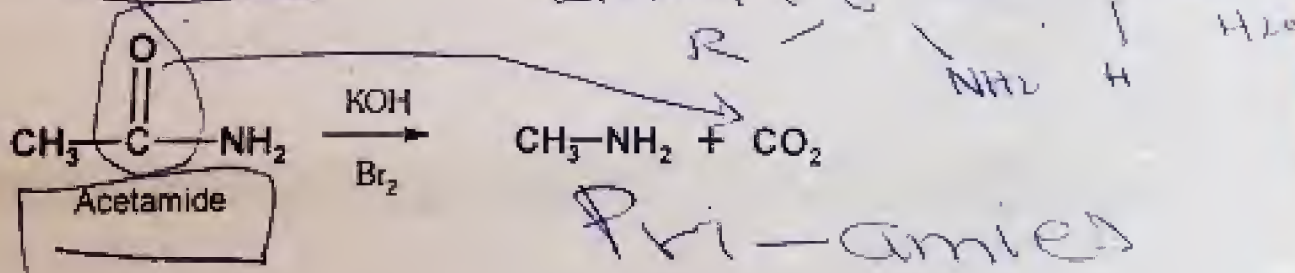


## (iii) REDUCTION OF AMIDES

- The amides can be reduced to amines by reducing agents



- An amide on treatment with Bromine in the presence of KOH yields primary amines.
- The reaction occurs through rearrangement.





**Exercise Q 3 (ix)** What are the main features which increase the basicity of amine?

**REACTIVITY/BASICITY:**

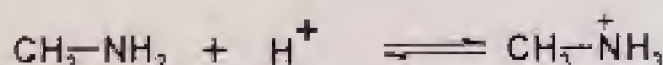
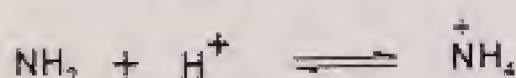
- Amines are basic and Nucleophiles because of non-bonding pair of electrons on nitrogen.

- The basicity depends upon

(i) relative availability of electron pair

(ii) the relative stability of corresponding ammonium ion.

Consider the following reactions.



The strength of a base is expressed in terms of  $pK_b$ , i.e.

$$pK_b = -\log K_b$$

*Handwritten notes:*  
 $pK_b \downarrow \Rightarrow$  basic strength  $\uparrow$   
 $pK_b \uparrow \Rightarrow$  basic strength  $\downarrow$   
 (vise versa)  
 For acid

For ammonia and methyl amine, the  $pK_b$  values are

$$pK_{\text{NH}_3} = 4.76 \quad ; \quad pK_{\text{CH}_3\text{NH}_2} = 3.38$$

Since  $pK_{\text{NH}_3} > pK_{\text{CH}_3\text{NH}_2}$ , methyl amine is a stronger base than ammonia.

It is due to two factors

- In ammonia, the lone pair of electron is attracted by s-orbitals of hydrogen atoms. The  $\text{CH}_3$  (alkyl) group has electron donating ability. Hence, in  $\text{CH}_3\text{NH}_2$ ,  $\text{sp}^3$ -orbitals of carbon pushes electrons towards nitrogen. Therefore, the pair of electron on nitrogen is relatively more available in methyl amine than in ammonia.

- The methyl ammonium ion,  $\text{CH}_3\text{NH}_3^+$  is stabilized due to electron donating inductive effect of the methyl group. On the other hand,  $\text{NH}_4^+$  ion is not stabilized by hydrogen atoms, since lone pair of nitrogen has been used up.

Both these factors favor methylamine to a stronger base than ammonia.

- Higher members show deviation from this behaviour.

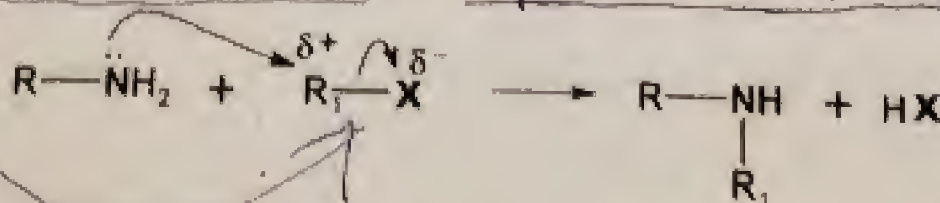
It is because the stabilization of a positive ion depends upon solvation, hydrogen bonding and resonance stabilization. Large size alkyl ammonium ions are less solvated. Also, large large size alkyl groups are highly non-polar, so the solvation decreases in water.

- Moreover, the availability of non-bonding pair of electrons is also affected by steric factor in addition to these aspects.

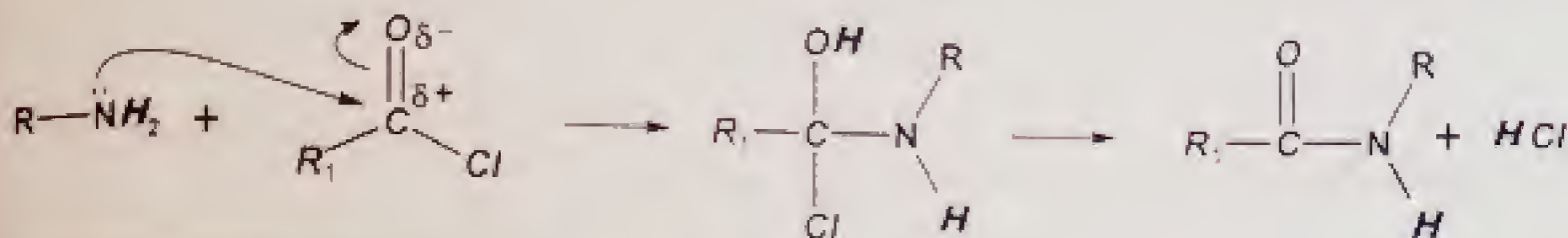
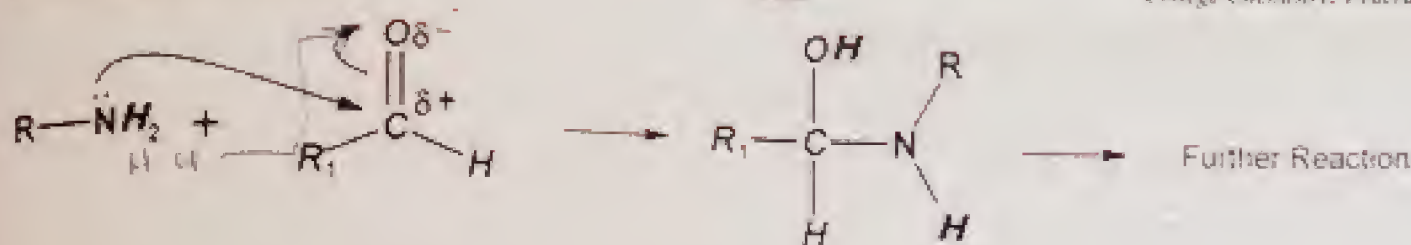
**REACTIONS OF AMINES**

The important organic reactions of amines (nucleophiles) are with the common electrophiles:

- Alkyl halides via nucleophilic substitution
- Aldehydes or ketones via nucleophilic addition
- Carboxylic acid derivatives, especially acid chlorides or anhydrides, via nucleophilic acyl substitution



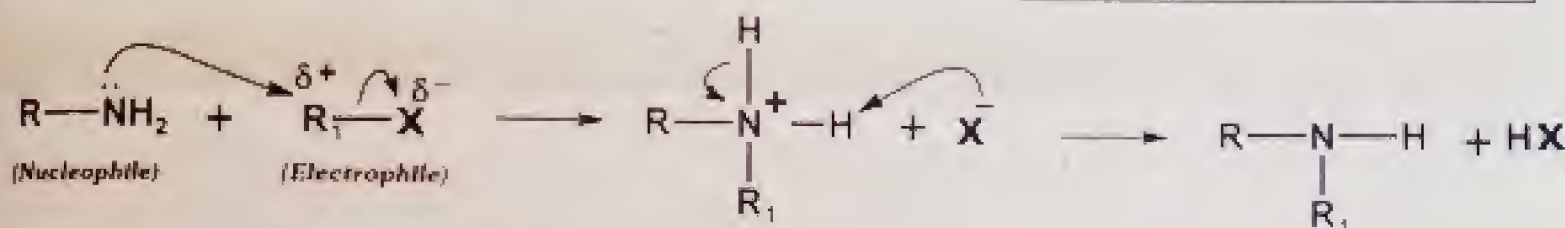




### (i) ALKYLATION OF AMINE BY ALKYL HALIDES

The alkylation of amines is called alkylation. It produces sec- or tertiary amines.

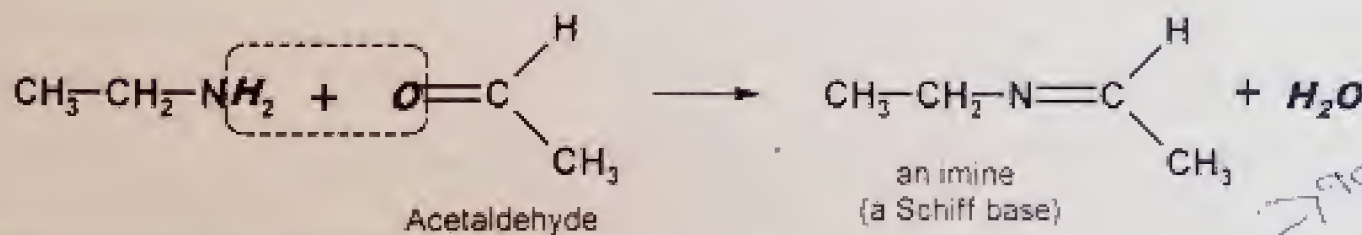
Same Reaction as on page 246



$R_2NH_2^+$  loses a proton with a base to give a free amine.

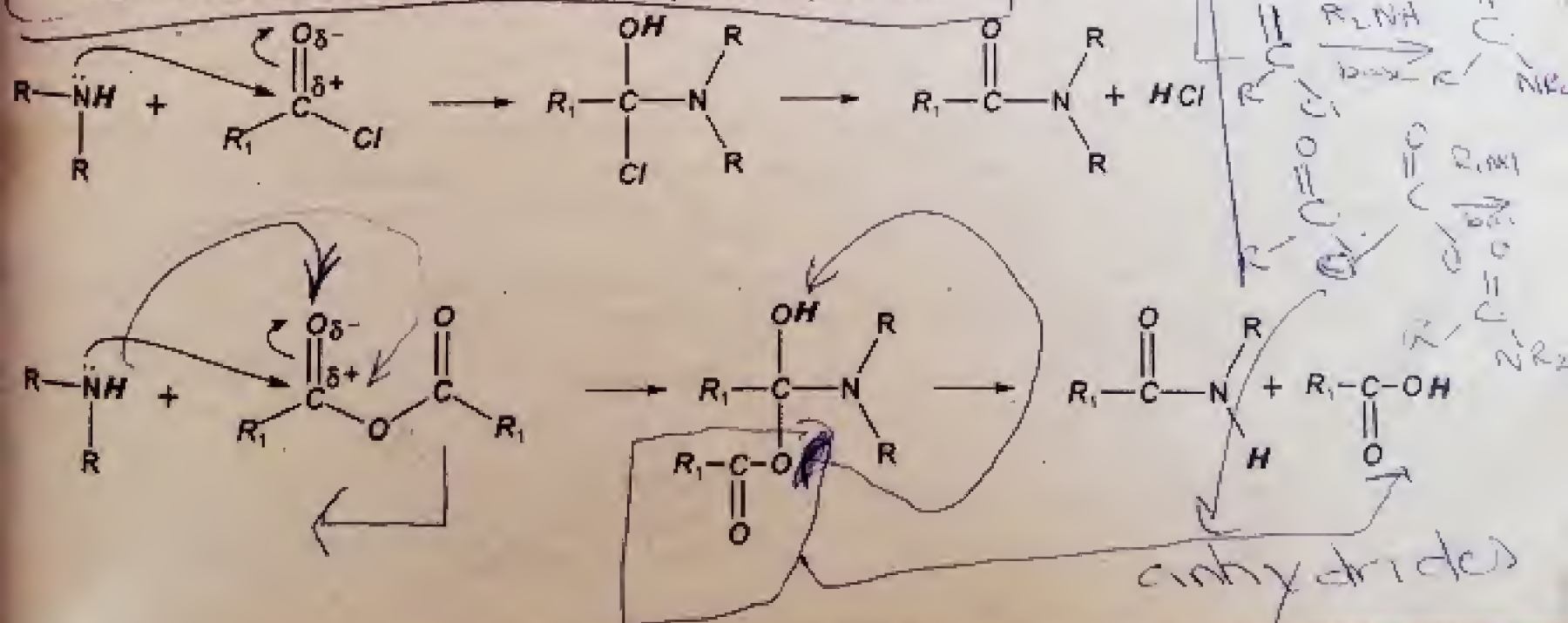
### (ii) REACTIONS OF PRIMARY AMINES WITH ALDEHYDES AND KETONES

Aldehydes and ketones react with primary amines to form Schiff's base.



### (iii) PREPARATION OF AMIDES

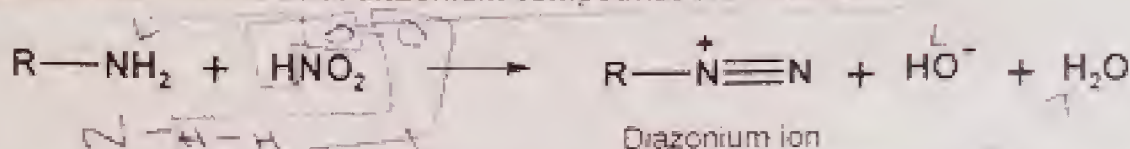
The amines react with acid halides and acid anhydrides to give amides.



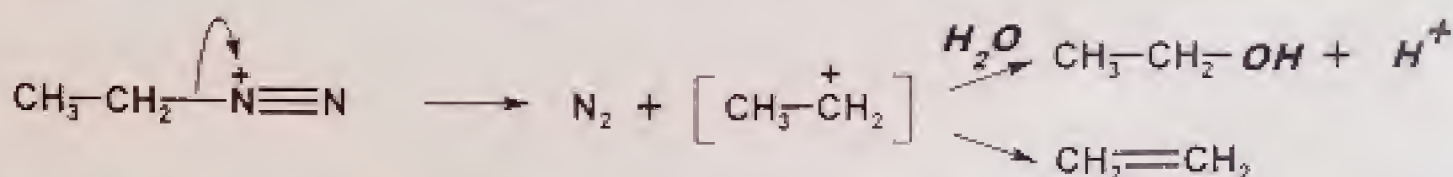


### (iv) PREPARATION OF DIAZONIUM SALTS

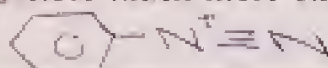
When amines react with nitrous acid, diazonium compounds are formed.



The diazonium group, group is rather unstable. In the case of the ethyldiazonium ion, it decomposes at once



When the group is attached to a benzene ring, through, the ion is stabilized to some extent by the delocalization of the ring. The benzenediazonium ion is therefore much more stable than its aliphatic counterpart. Nevertheless, it decomposes readily above 10°C.



### QUICK QUIZ-3

#### (1) Define hydration

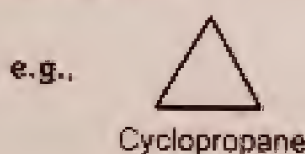
The addition of water to a substance is called hydration.

**Example:** The addition of water to alkenes gives alcohols

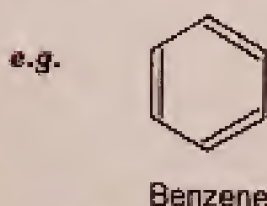
#### (2) What is the difference between alicyclic and aromatic compounds

Non-benzenoid cyclic hydrocarbons are alicyclic hydrocarbons.

Alicyclic hydrocarbons possess two hydrogen atoms less than their corresponding open chain hydrocarbons.



Benzenoid cyclic hydrocarbons are known as aromatic hydrocarbons.

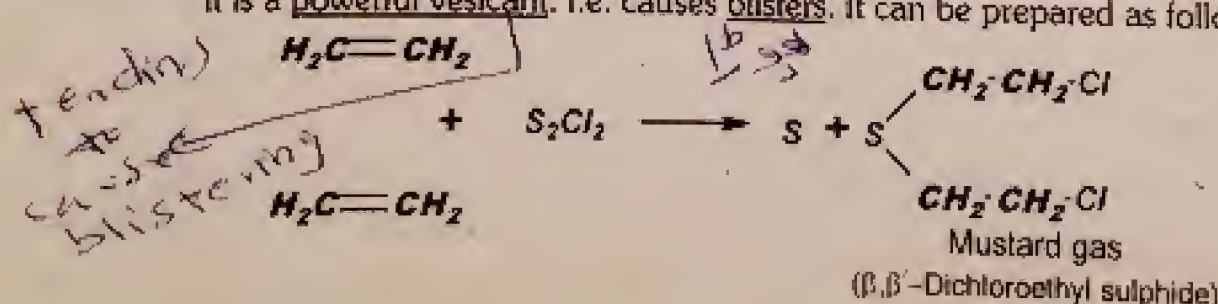


#### (3) Define IUPAC

IUPAC stands for International Union of Pure and Applied Chemistry. The IUPAC is the accepted authority for chemical standards of nomenclature, measurements, and atomic mass values.

#### (4) Write the equation for the preparation of mustard gas

Mustard gas is actually a high boiling liquid and has mustard like odour. It was used in World War I, because it is a powerful vesicant, i.e. causes blisters. It can be prepared as follows.





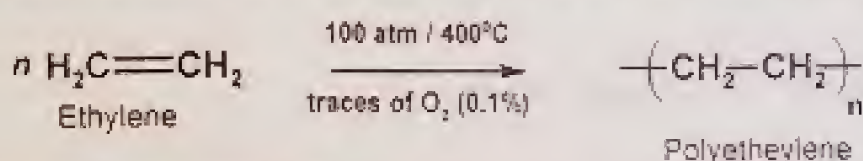
**(5) Define polymers**

Polymerization is a process in which a small organic molecules which are called monomers combine together to form larger molecules. The substances so produced are called polymers.  
e.g. Polyethene, Polyvinyl chloride (PVC)

**(6) What is polymerization**

Polymerization is a process in which a small organic molecules which are called monomers combine together to form larger molecules. The substances so produced are called polymers.

e.g.

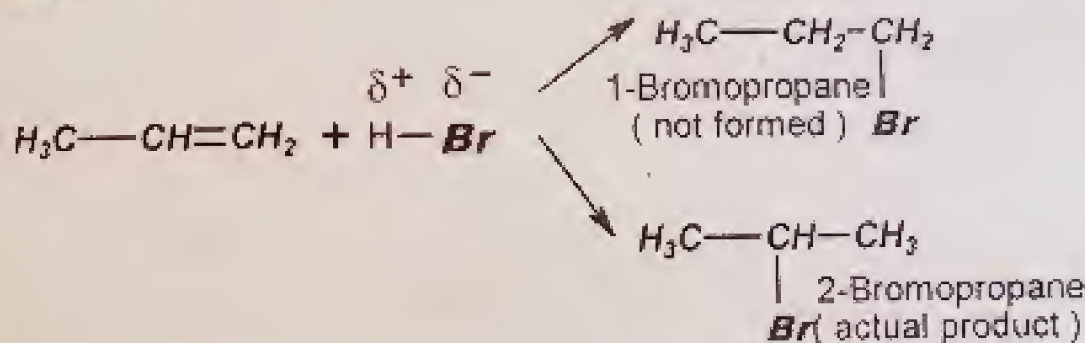


**(7) What is Markownikov's rule?**

It states

In the addition of an unsymmetrical reagent to an unsymmetrical alkene, the negative part of the adding reagent goes to that carbon, consisting the double bond, which has least number of hydrogen atoms.

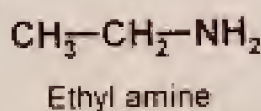
Example:



**(8) What are amines**

The organic compounds containing  $\text{NH}_2$  functional groups are called amines.

Examples:



\* vinyl or ethenyl is the functional group  $-\text{CH}=\text{CH}_2$

**(9) Why halogen of vinyl chloride is inert?**

Halogen atom has lone pair of electrons which come in resonance with the double bond of vinyl group.



Thus, the C to Cl bond develops some double bond character in it. Therefore, it becomes very much difficult to displace this Cl atom by any nucleophile. Hence, the halogen atom of vinyl chloride is inert in substitution reactions.

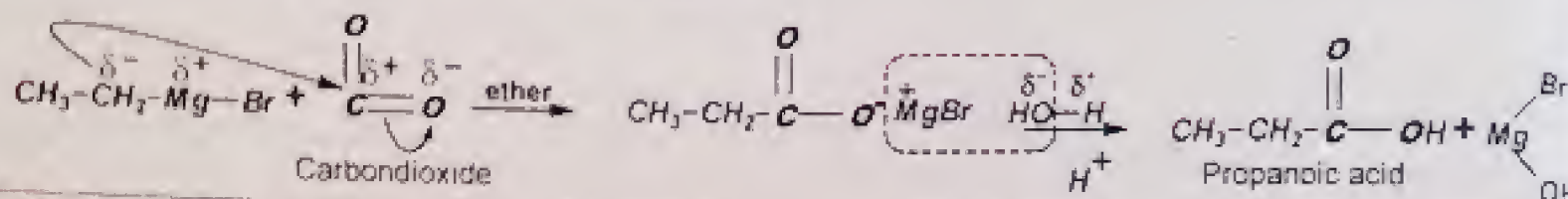
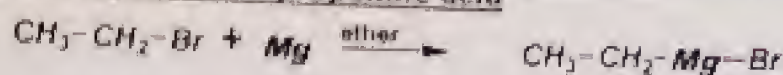
**Do You Know?**

- (i) CD's are made from vinyl chloride
- (ii) Ethyl chloride is used as a typical anesthetic
- (iii) Erupting volcanoes emit large quantities of halogens and halides

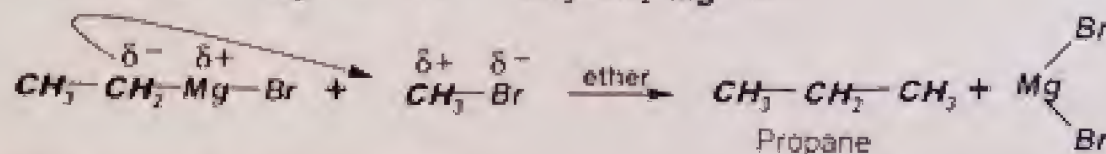
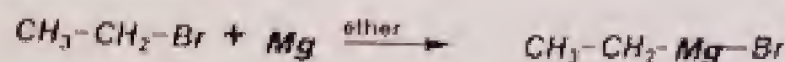


## SOME IMPORTANT CONVERSIONS

### (i) Ethyl bromide to propanoic acid



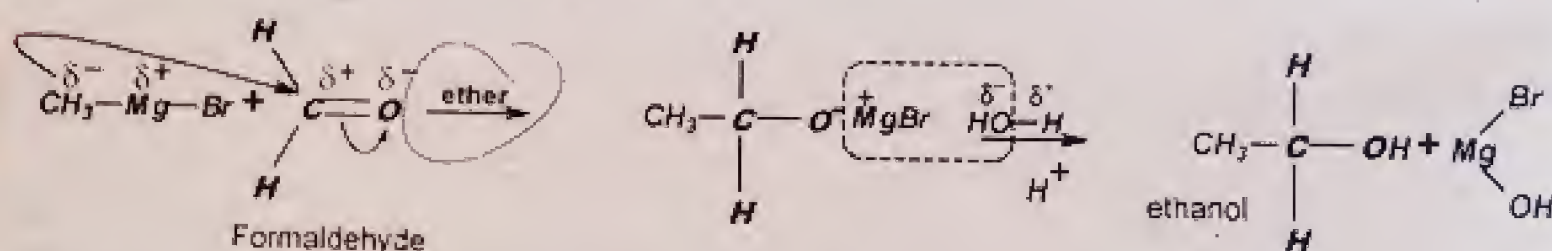
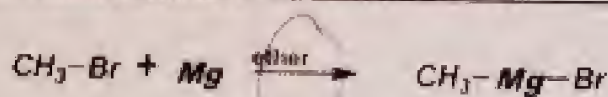
### (ii) Ethyl bromide to propane



### (iii) Ethyl bromide to Ethyl cyanide

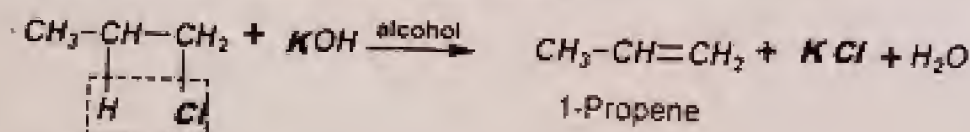


### (iv) Methyl bromide to Methyl alcohol

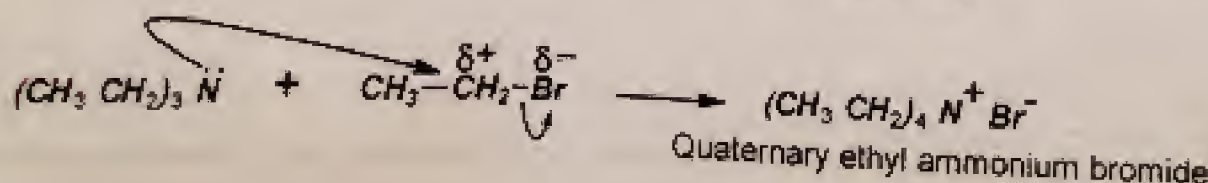
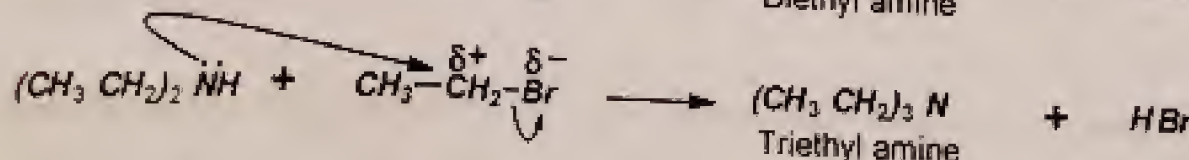
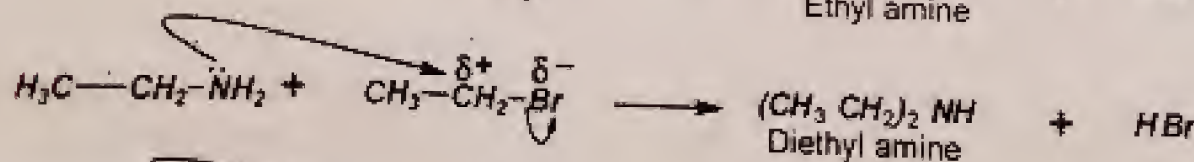


Similarly secondary and tertiary alcohols can be prepared

### (v) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ to $\text{CH}_3\text{-CH=CH}_2$



### (vi) $\text{CH}_3\text{-CH}_2\text{-Br}$ to $(\text{CH}_3\text{-CH}_2)_4\text{N}^+\text{Br}^-$



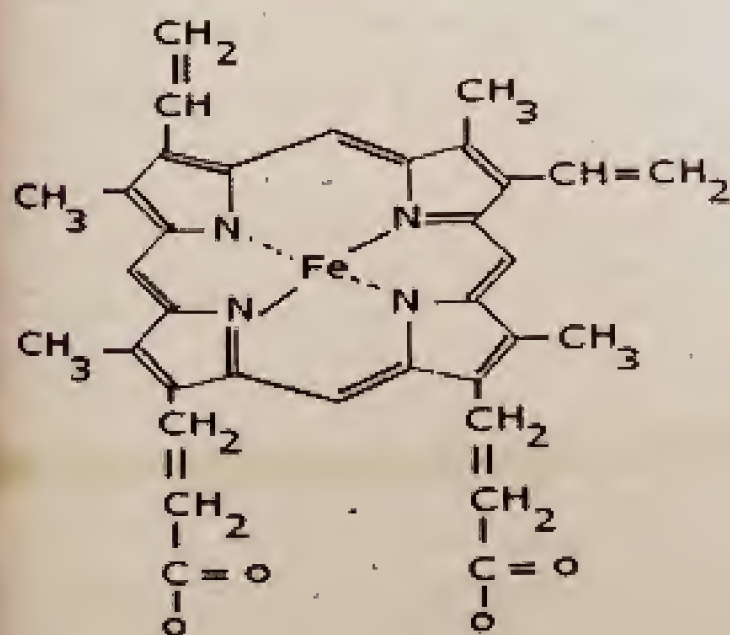


## ORGANOMETALLIC COMPOUNDS IN MEDICINES

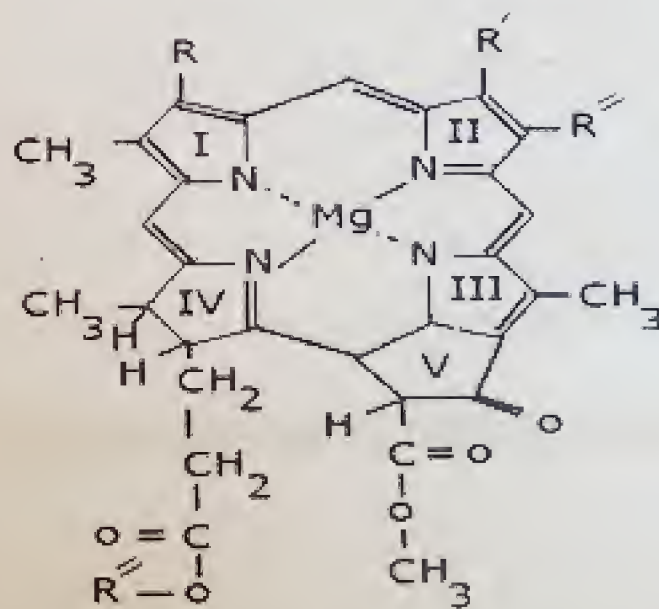
- Cisplatin ( $\text{C}_2\text{H}_4)_2\text{PtCl}_2$  displays anti-cancer activity in chemotherapy
- Arene- and cyclopentadienyl complexes are kinetically inert platforms for the design of new radiopharmaceuticals.
- Mercurochrome (Merbromin) is an over-the-counter topical antiseptic.
- Merthiolate (Thiomersal) has applications as an antifungal and antiseptic agent. This compound is also used as a vaccine preservative, in immunoglobulin preparations and nasal products
- Salvarsan (arsphenamine in the States) is an anti-sypilis medication.
- Titanocene dichloride,  $\text{Cp}_2\text{TiCl}_2$  has shown significant anticancer attributes
- Tamoxifen is an anticancer compound.
- Ferrocenyl derivative chloroquine is an antimalarial compound.
- Titanocene dichloride,  $(\text{Cp})_2\text{V}(\text{NCS})_2$ , and carboplatin are anticancer drugs.
- Ferroquine, a combination of ferrocene and chloroquine, is antimalarial drug
- Vanadocene acetylacetonate has potential in preventing HIV transmission.
- Ru ( $\eta^6\text{-C}_6\text{H}_6$ )  $\text{Cl}_2$  (DMSO) has been shown to inhibit topoisomerase II, an important target in chemotherapy.

Hemoglobin and chlorophyll both are natural organo-metallic compounds. Both consist of a substituted porphyrin ring coordinated with a metal ion.

- (1) Hemoglobin is a porphyrin ring with iron while chlorophyll is a porphyrin ring with magnesium.
- (2) Hemoglobin is the red pigment in the blood while chlorophyll is the green pigments in green plants, algae, and certain organism.
- (3) Hemoglobin is involved in oxygen transport while chlorophyll functions as a receptor of light energy during photosynthesis.



### Structure of Heme



### Structure of Chlorophyll



## KEY POINTS

- Monohalo derivatives of alkanes are called alkyl halides.
- The general formula of alkyl halides is  $C_nH_{2n+1}X$ .
- The best method for the preparation of alkyl halides is by the reactions of alcohols with inorganic halides like  $SOCl_2$ ,  $PX_3$  and  $PX_5$ .
- Alkyl halides are very reactive class of organic compounds. They undergo nucleophilic substitution reaction and elimination reaction in the presence of a nucleophile or a base.
- Nucleophilic substitution reactions can take place in two distinct ways. A one step mechanism is called  $S_N2$  while a two step mechanism is called  $S_N1$ .  $S_N1$  reaction shows first order kinetics whereas  $S_N2$  reaction shows  $2^{nd}$  order kinetic.
- Nucleophilic substitution reactions take place simultaneously with elimination reaction and often compete with them.
- Elimination of two atoms or groups from adjacent carbon atoms in the presence of a nucleophile or a base is called elimination reaction. Like nucleophilic substitution,  $\beta$ -elimination reactions also take place in two distinct ways E2 and E1.
- A nucleophile is an electron rich species that will react with an electron poor species.
- A substitution implies that one group replaces another.
- Grignard reagent can be prepared by adding alkyl halide in a stirred suspension of magnesium metal in diethyl ether.
- Grignard reagent has a reactive nucleophilic carbon atom which can react with electrophilic centered to give the products in high yields. Primary, secondary and tertiary alcohols can be best prepared by reacting Grignard reagent with formaldehyde, any other aldehydes and ketones, respectively.
- The polar nature of the N-H bond (due to the electronegativity difference of the two atoms) results in the formation of hydrogen bonds with other amine molecules.
- Primary amines,  $R-NH_2$  or  $ArNH_2$ , undergo nucleophilic addition with aldehydes or ketones to give **carbinolamines** which then dehydrate to give substituted **imines**.
- **Primary alkyl or aryl amines** yield **diazonium salts**.



## EXERCISE

**Q1: Select the right answer from the choices given with each question.**

(i) In primary alkyl halides, the halogen atom is attached to a carbon which is further attached to how many carbon atoms;

- (a) Two (b) Three (c) One (d) Four

(ii)  $S_N2$  reactions can be best carried out with:

- (a) Primary alkyl halides (b) Secondary Alkyl halides (c) Tertiary alkyl halides (d) All the three

(iii) For which mechanisms, the first step involved is the same;

- (a)  $E_1$  and  $E_2$  (b)  $E_2$  and  $SN_2$  (c)  $E_1$  and  $SN_2$  (d)  $E_1$  and  $SN_1$

(iv) The rate of  $E_1$  reaction depends upon;

- (a) the concentration of substrate (b) the concentration of nucleophile.  
(c) the concentration of substrate as well as nucleophile (d) None of the above.

(v) Alkyl halides are considered to be very reactive compounds towards nucleophiles, because:

- (a) they have an electrophilic carbon  
(b) they have an electrophilic carbon and a good leaving group  
(c) they have an electrophilic carbon and a bad leaving group  
(d) they have a nucleophilic carbon and a good leaving group

(vi) Which one of the following is not a nucleophile:

- (a)  $H_2O$  (b)  $H_2S$  (c)  $BF_3$  (d)  $NH_3$

(vii) Double bond is formed as a result of:

- (a) Substitution reactions (b) Elimination reactions  
(c) Addition reactions (d) Rearrangement reactions

(viii) Which of the following alkyl halides cannot be formed by direct reaction of alkanes with halogen

- (a)  $RBr$  (b)  $RCI$  (c)  $RF$  (d)  $RI$

(ix)  $CH_3CH_2Br$  on treatment with alc.  $KOH$  gives:

- (a) Propanal (b) Propene (c) Propane (d) None

(x) Grignard's reagent gives alkane with:

- (a) Water (b) Ethylamine (c) Ethanol (d) All of these

(xi) Action of alkyl halides with Na metal yield;

- (a) Alkanes (b) Alcohols (c) Alkenes (d) Phenols

(xii) Alkyl halides react with excess of ammonia to give;

- (a)  $1^\circ$ -amine (b)  $2^\circ$ -amine (c)  $3^\circ$ -amine (d) all

(xiii) Among the alkyl halides the primary alkyl halides always follow the mechanism:

- (a)  $SN_1$  (b)  $SN_2$  (c)  $SN_3$  (d)  $SN_4$

(xiv) Grignard's reagent on treatment with chloramines gives;

- (a) Acetamide (b) Primary amine (c) Secondary amine (d) urea

(xv) Nucleophilic addition of a primary amine giving;

- (a) Imine (b) urea (c) ammonia (d) Nitrobenzene

## ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (c) One

By definition, the primary carbon atom is directly attached to one carbon atom. e.g. in  $CH_3-CH_2-Br$ , the carbon atom attached to Br is the primary carbon atom.

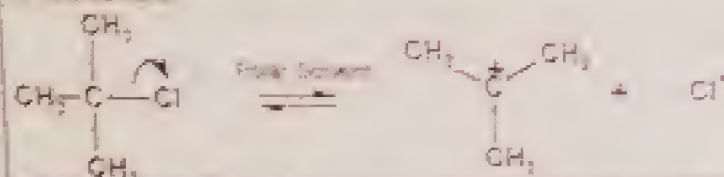
(ii) Ans: (a) Primary alkyl halides

Since primary alkyl halides have less steric hinderance. So, the nucleophile can easily attack and the leaving group leaves in one step. Such type of reaction is  $S_N2$ .



**(iii) Ans: (d) E1 and S<sub>N</sub>1**

The first step both E1 and S<sub>N</sub>1 reaction is the formation of carbocation.



**(iv) Ans: (a) the concentration of substrate**

E1 reaction is a two-step reaction. The first step is slow, involves substrate only. So, the rate depends upon concentration of substrate only.  
i.e. Rate = k [substrate]

**(v) Ans: (b) they have an electrophilic carbon and a good leaving group.**

In alkyl halides, the carbon attached to halogen is electrophilic. Moreover, halogens are good leaving group as well except F. So, they are very reactive towards nucleophiles.

**(vi) Ans: (c) BF<sub>3</sub>**

H<sub>2</sub>O, H<sub>2</sub>S and NH<sub>3</sub> all contain lone pair of electron, they are nucleophiles.  
In BF<sub>3</sub>, the Boron has six electron in its octet, so it is electron deficient. Hence, it cannot act as nucleophile. Instead it can behave as electrophile since it can accept electrons to complete its octet.

**(vii) Ans: (b) Elimination reactions**

Elimination reaction gives alkenes.

e.g. dehydrohalogenation of alkyl halides

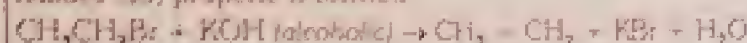


**(viii) Ans: (d) RI**

The reaction of alkane with I<sub>2</sub> form HI which is a strong reducing agent. It reduces the alkyl halide back to alkane.  
 $\text{CH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{I} + \text{I}$   
 $\text{CH}_3\text{I} + \text{HI} \rightarrow \text{CH}_4 + \text{I}_2$

**(ix) Ans: (b) Propene**

Alcoholic KOH brings about the dehydrohalogenation of alkyl halides. So, propene is formed.

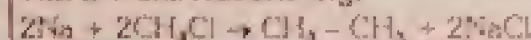


**(x) Ans: (d) All of these**

Grignard reagent is R<sup>-</sup> - Mg - X. Since, water (H<sub>2</sub>O), amine (C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>) and ethanol (C<sub>2</sub>H<sub>5</sub>OH) all contain H-atom. Thus, Grignard reagent can take hydrogen from these compounds to form alkanes (i.e., RH).

**(xi) Ans: (a) Alkanes**

This is Wurtz reaction. e.g.,



**(xii) Ans: (d) all**

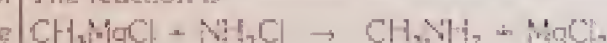
All types of amines are produced depending upon the no. of reactants.

**(xiii) Ans: (b) S<sub>N</sub>2**

Primary alkyl halides have no hinderance to the approach of nucleophile. Therefore, the attack of a nucleophile and the removal of the leaving group take place in one step. So, this is the S<sub>N</sub>2 reaction.

**(xiv) Ans: (a) 1°-amine**

The reaction is



**(xv) Ans: (a) Imine**

Nucleophilic addition of amine to carbonyl compounds give imine (See next chapter)

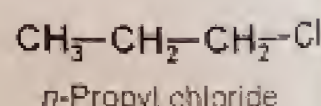
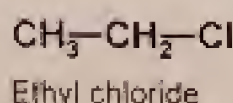
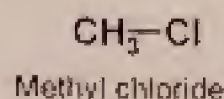
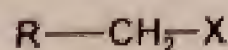
**Q2: Give brief answers for the following questions.**

(i) What are primary, secondary and tertiary alkyl halides?

(i) **Primary Alkyl Halides:**

Alkyl halide in which halogen atom is attached with primary carbon are called primary halides.

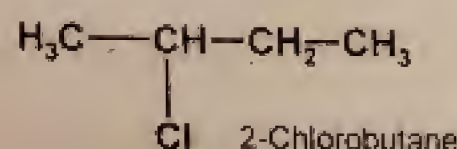
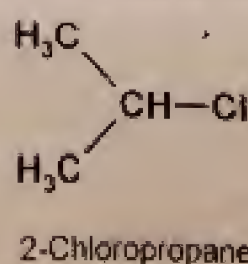
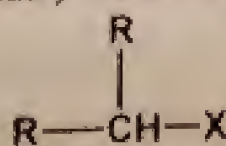
A primary C-atom is attached to one or no carbon atom is called a primary C-atom.



(ii) **Secondary Alkyl Halides:**

Alkyl halide in which halogen atom is attached with a secondary carbon atom is called secondary alkyl halide.

A Secondary C-atom is attached to two C-atoms simultaneously is called a secondary C-atom.

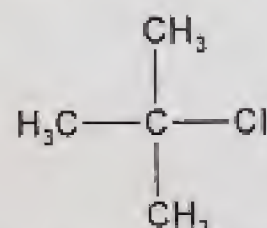
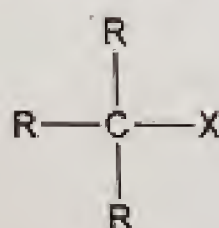




**(III) Tertiary Alkyl Halides:**

Alkyl halides, in which halogen atom is attached to a tertiary carbon is called tertiary alkyl halide.

A tertiary C-atom is attached to three C-atoms simultaneously is called a tertiary C-atom.

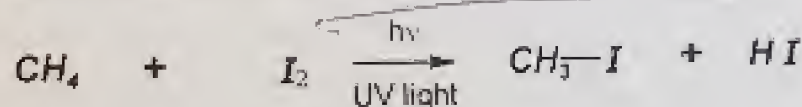


2-Chloro-2-methylpropane

**(II) Why alkyl iodides cannot be prepared by directly heating iodine with alkane?**

The alkyl iodides cannot be obtained directly by treating alkanes with iodine.

It is because when an alkane reacts with iodine, alkyl iodide and HI are produced. The HI is a strong reducing agent. So, it reduces the product alkyl iodide back to the original alkane.



**(III) What are Nucleophilic substitution reactions or S<sub>N</sub> reaction?**

The reaction in which a nucleophile replaces another atom or a group of atom already present in a molecule are called nucleophilic substitution reactions.

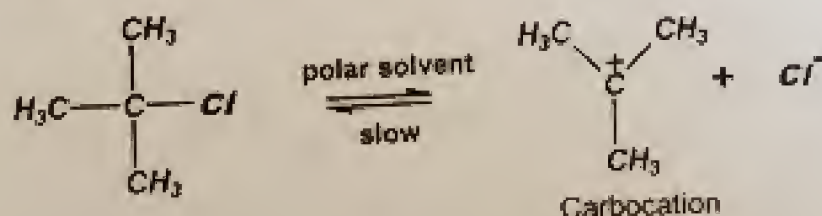
General process of S<sub>N</sub> reactions is



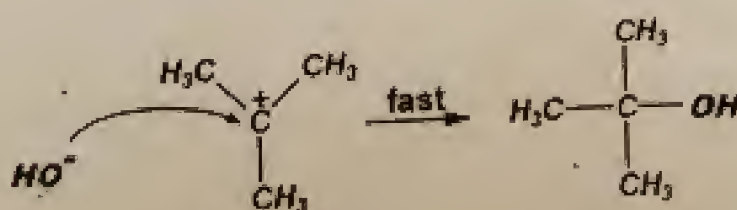
**(iv) Tertiary alkyl halides show S<sub>N</sub>1 reactions mostly, why?**

- In tertiary alkyl halides, the tertiary carbon atom is surrounded by bulky alkyl groups. Therefore, it is difficult for a nucleophile to reach this carbon. Hence, S<sub>N</sub>2 reaction cannot occur with tertiary alkyl halides.
- The tertiary alkyl halides first undergo ionization. During this process leaving group leaves and the tertiary carbon becomes sp<sup>2</sup>-hybridized with angle 120°. Thus, nucleophile easily attacks the tertiary carbon atom. Therefore, S<sub>N</sub>1 reaction occurs with tertiary alkyl halides. The reaction complete in two steps.

Step - 1



Step - 2





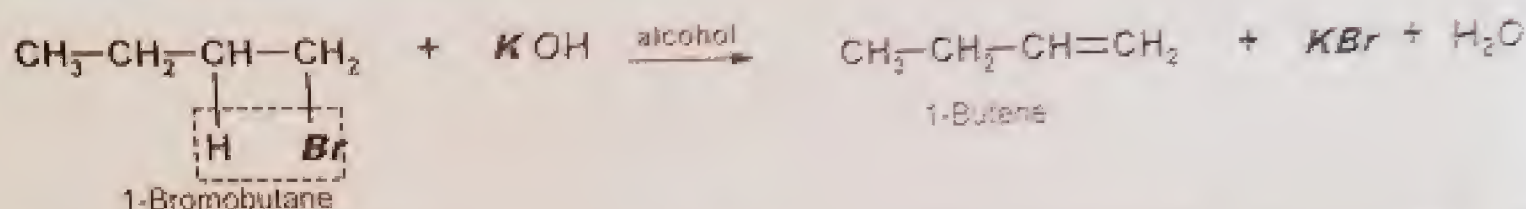
(e) What are elimination reactions?

The chemical reaction in which two groups are eliminated without being replaced from a molecule is called elimination reaction.

When  $\beta$ -hydrogen is eliminated, it is called  $\beta$ -elimination reaction.

**Examples:**

Alkyl halides on heating with alcoholic potassium hydroxide undergo dehydrohalogenation to form alkenes.



(ul) Which factor decides the reactivity of alkyl halides?

There are two main factors which control the reactivity of alkyl halides:

(i) **Bond Polarity**

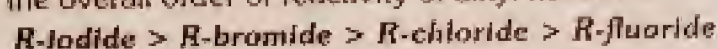
The molecule of alkyl halide is polarized due to the greater electronegativity of halogens as compared to C. Hence carbon acquires partial positive whereas halogens acquires partial negative charge. Halogen becomes nucleophilic in character, which can be replaced by another nucleophile.

(ii) **Bond Energy**

Experiments have shown that the bond energy of C-X bond is the main factor which decides the reactivity of alkyl halides, and not the polarity of the molecule.

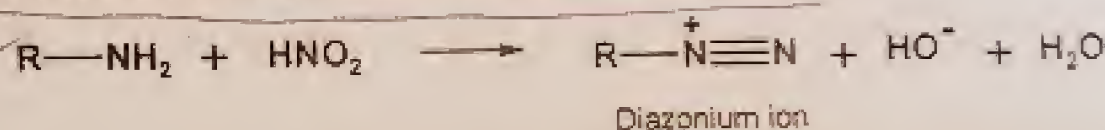
A study of bond energies of C-X bond shows that C-F bond is the strongest.

So the overall order of reactivity of alkyl halides is:

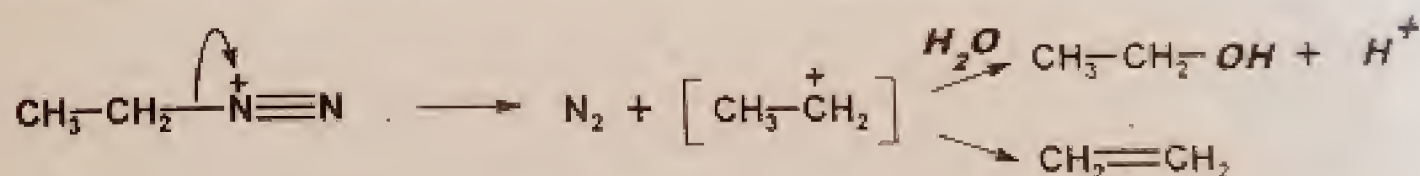


(ult) What are the diazonium salt?

When amines react with nitrous acid, diazonium compounds are formed.



The diazonium group, group is unstable. In the case of the ethyldiazonium ion, it decomposes at once:

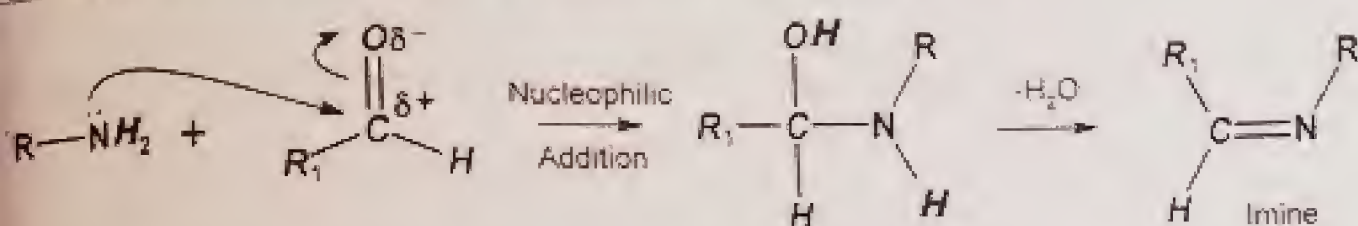


When the group is attached to a benzene ring, the ion is stabilized to some extent by the delocalized electron of the ring. The benzenediazonium ion is therefore much more stable than aliphatic. However, it also decomposes readily above  $10^\circ\text{C}$ .





(viii) How can nucleophilic addition of a primary amine giving an imine?

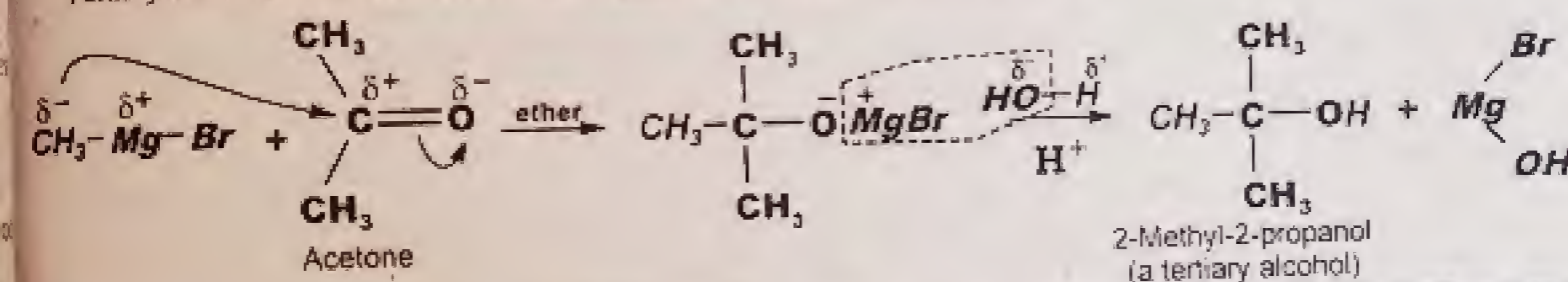


(ix) Amines are more basic than analogous alcohols why?

Amines may act as bases towards acids. They are more basic than alcohols and ethers. It is because they have single electron pair on nitrogen atom which is readily donated. On the other hand, in alcohols, there are two lone pairs of electrons on oxygen atom. These two electrons compete with each other during donation. Hence, neither of these two is readily donated, so alcohols are weaker bases than amines.

(x) How tertiary alcohols are obtained from R-Mg-X?

Tertiary alcohols are obtained by the reaction of R-Mg-X with ketones. e.g.



Q3: Give detailed answers for the following questions.

(i) Discuss the reactivity of alkyl halides.

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(ii) Give three methods for the preparation of alkyl halides.

Page 226

(iii) Explain in detail  $S_N1$  and  $S_N2$  reactions with mechanism.

Page 231

(iv) What are  $\beta$ -elimination reactions? Explain them with detail.

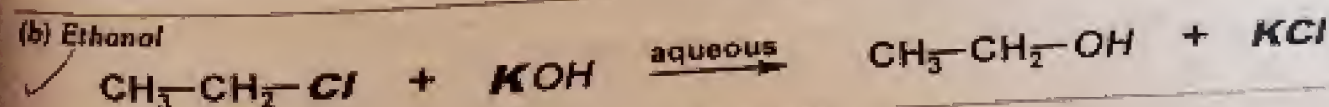
Page 234

(v) How will you convert ethyl chloride to the

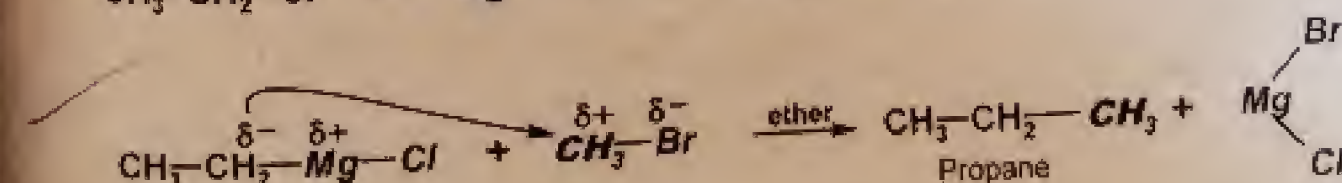
(a) Ethyl cyanide



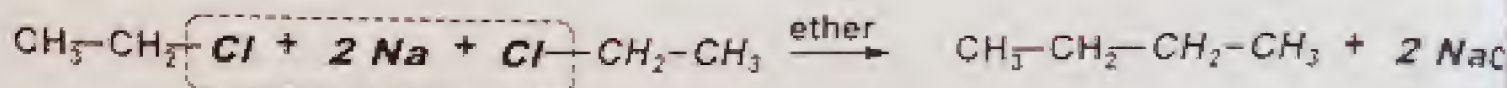
(b) Ethanol



(c) Propane





(d) *n*-Butane

(d) Tetraethyl lead.



(vi) Discuss the preparation and reactivity of Grignard's reagent.

Page 240

(vii) What are the amines? Give its nomenclature.

Page 244

(viii) What are the main features which increase the basicity of amine?

Page 250

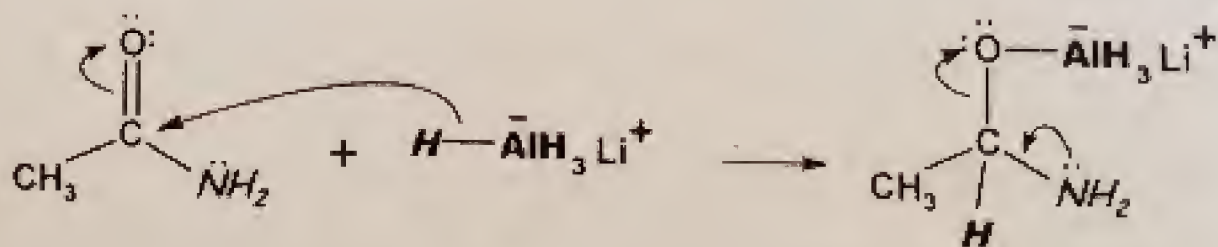
(ix) Amides are reduced by  $\text{LiAlH}_4$ . Give mechanism.

## Reaction:



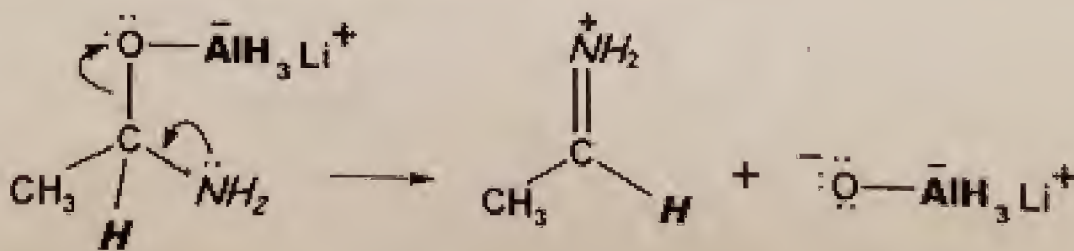
### Mechanism

- The nucleophilic H from the hydride reagent adds to the electrophilic C in the polar carbonyl group of the amide.
- The electrons from the C=O move to the electronegative O creating an intermediate metal alkoxide complex.



**Step 2:**

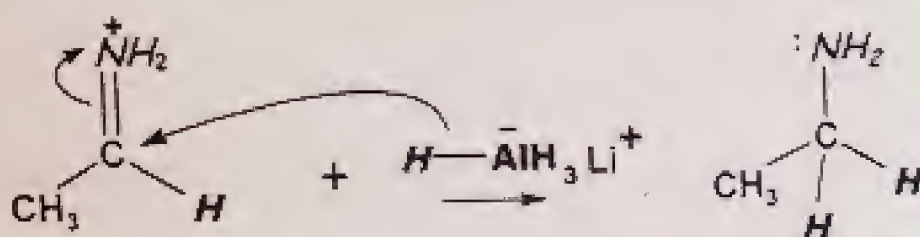
- The tetrahedral intermediate collapses and displaces the O as part of a metal alkoxide leaving group
- This produces a highly reactive iminium ion an intermediate.





Step 3:

- The nucleophilic H from the hydride reagent adds to the electrophilic C in the iminium system.
- The  $\pi$ -electrons from the C=N move to the cationic N to neutralize the charge. Thus amine is produced.

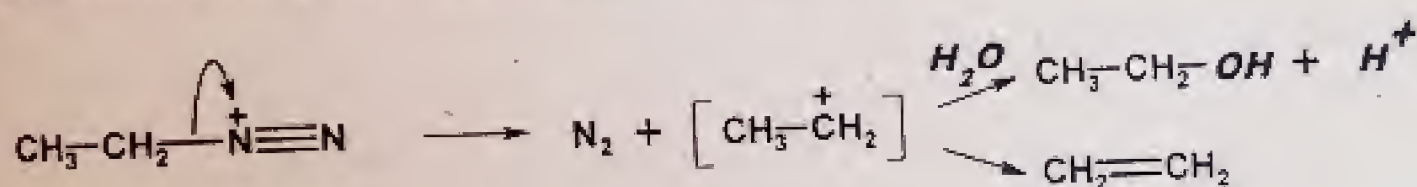


(x) What are the diazonium salts? How they can be prepared? Give their reactions?

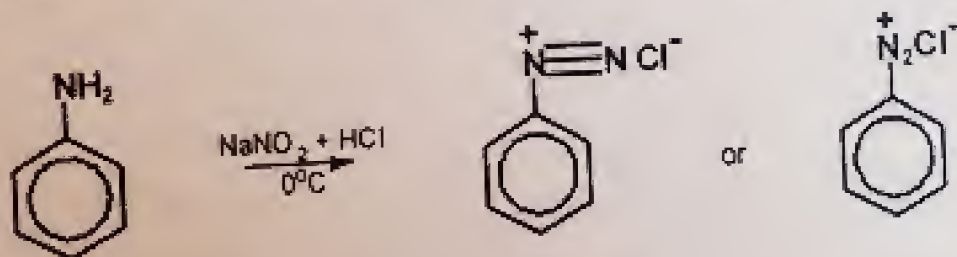
When amines react with nitrous acid, diazonium compounds are formed.



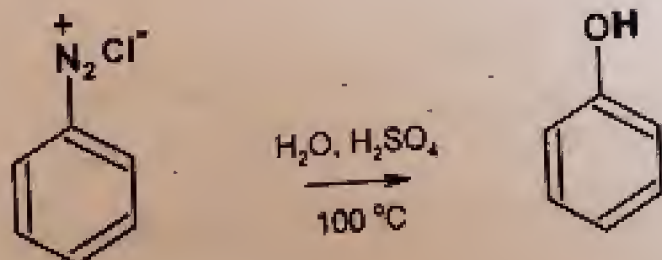
The diazonium group, group is rather unstable. In the case of the ethyldiazonium ion, it decomposes at once:



When the group is attached to a benzene ring, the ion is stabilized to some extent by the delocalized electron of the ring. The benzenediazonium ion is therefore much more stable than aliphatic. However, it also decomposes readily above  $10^\circ C$ .



Reactions





**TEST YOUR SKILLS**

**Marks: 85**

**OBJECTIVE**

**Time: 20 Minutes**

**Marks: 17**

**Note:** Over writing, cutting, erasing, using lead pencil will result in loss of marks

**Q1. Circle the correct option i.e. A/B/C/D. Each part carries one mark.**

- (i)  $C_2H_5Br + NaOH \longrightarrow C_2H_5OH + NaBr$ , the reaction is  
A. Electrophilic    **B. Nucleophilic**    C. Both    D. None
- (ii) In  $CH_3COCH_3 + CH_3MgI \longrightarrow$  Intermediate  $+ H_2O \longrightarrow X$   
This X is  
A.  $CH_3OH$     B.  $C_2H_5OH$     C.  $CH_3CN$     **D. Tertiary butyl alcohol**
- (iii) Which reagent cannot be used for preparation of alkyl halides from alcohols?  
A.  $HCl + ZnCl_2$     **B. NaCl**    C.  $PCl_5$     D.  $SOCl_2$
- (iv) Treatment of ammonia with excess of ethyl chloride will yield  
A. Diethyl amine    B. Ethane    C. Methyl amine    **D. Tetraethyl ammonium chloride**
- (v) Alkyl fluorides are less reactive than alkyl iodides due to  
**A. high bond energy**    B. low bond energy    C. high bond polarity    D. low bond polarity
- (vi) For the reaction  $C_2H_5OH + HX \longrightarrow C_2H_5X$   
The order of reactivity is  
A.  $HBr > HI > HCl$     **B.  $HI > HBr > HCl$**     C.  $HI > HCl > HBr$     D.  $HCl > HBr > HI$
- (vii) When ~~ethyl~~ magnesium bromide is treated with ethylene oxide the product is  
A. 2-butanol    **B. 1-butanol**    C. Both    D. None
- (viii) Grignard reagent is  
A. Organo-cupric compounds    **B. Organo-magnesium compounds**  
C. Organo-zinc compounds    D. None of above
- (ix) Which one of the following is an electrophile?  
A.  $NH_3$     B.  $H_2O$     C.  $Cl_2$     **D.  $BF_3$**
- (x) What is shape of carboxation?  
A. Linear    B. Planar Square    **C. planar**    D. Tetrahedral
- (xi) Double bond is formed as result of  
A. Substitution reaction    **B. Elimination reactions**  
C. Addition reactions    D. Rearrangement reaction
- (xii) The common name of 2-methyl-2-chloropropane is  
A. Isobutyl chloride    B. sec-butyl chloride    **C. ter-butyl chloride**    D. n-butyl chloride
- (xiii) E2 reaction obeys  
A. First order kinetics    **B. Second order kinetics**    C. Third order kinetics    D. Zero order kinetics
- (xiv) Which of the following alkyl halides cannot be formed by direct reaction of alkanes with halogen  
A.  $RBr$     B.  $RCI$     C.  $RF$     **D.  $RI$**
- (xv)  $CH_3CH_2Br$  on treatment with alc. KOH gives  
A. Propanal    B. Propene    C. Propane    **D. None**
- (xvi) Grignard's reagent gives alkane with  
A. Water    B. Ethylamine    C. Ethanol    **D. all of these**
- (xvii) Action of alkyl halides with Na metal yield  
**A. Alkanes**    B. Alcohols    C. Alkenes    D. Phenols

**SUBJECTIVE**

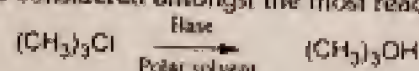
**Time: 2:35 Hours**

**Total Marks Section B and C: 68**

**Section - B (Marks 42) (14 × 3 = 42)**

**Q2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines.**

- (i) Alkyl halides are considered amongst the most reactive class of organic compounds. Consider the equation



- a. Suggest the name and mechanism involved for the above conversion. 01
- b. What will happen to the configuration of alkyl halide during the process? 01
- c. Write rate equation for this reaction. 01
- (ii) a. How does nature of alkyl group change when alkyl halide is converted into Grignard's reagent? 01
- b. Why is the dry ether necessary for the preparation of Grignard's reagent? 01
- c. How does the primary alcohol produce when ethylene oxide reacts with Grignard's reagent? 01
- (iii) How is Grignard Reagent used for the preparation of alkanes? Give any three examples with reaction.



- |            |  |    |
|------------|--|----|
| (iv) a.    | Write two methods for the preparation of alkyl halides?  | 03 |
| b.         | What are primary secondary and tertiary alkyl halides?   | 02 |
|            |  | 01 |
| (v) a.     | Why alkyl iodides cannot be prepared by directly heating iodine with alkenes?  | 01 |
| b.         | Thionyl chloride (SOCl <sub>2</sub> ) is the best reagent to get alkyl chlorides from alcohols why?  | 02 |
| (vi) a.    | How alkyl iodides are prepared?  | 01 |
| b.         | Which factor decides the reactivity of alkyl halides?  | 01 |
| c.         | Define an electrophile and a nucleophile.  | 01 |
| (vii) a.   | Explain the given order of reactivity<br>R-I > R-Br > R-Cl > R-F   | 03 |
| (viii) a.  | What products are formed when the following compounds are treated with Ethyl magnesium Bromide.<br>A. HCHO.      B. (CH <sub>3</sub> ) <sub>2</sub> CO | 02 |
| b.         | Why Grignard's reagent is highly reactive?   | 01 |
| (ix) a.    | What are Nucleophile substitution reactions or S <sub>N</sub> reactions?   | 01 |
| b.         | Why primary alkyl halides always follow S <sub>N</sub> 2 mechanism?  | 01 |
| c.         | Tertiary alkyl halides show S <sub>N</sub> 1 reactions mostly. Why?  | 01 |
| (x) a.     | S <sub>N</sub> 2 reactions shows 2 <sup>nd</sup> order kinetics, why?  | 01 |
| b.         | Why the configuration of the product is inverted during S <sub>N</sub> 2 mechanism?  | 01 |
| c.         | Why there is 50% inversion and 50% retention in the product formed during S <sub>N</sub> 1 reaction?   | 01 |
| (xi) a.    | Write down the t-butyl bromide with KOH in aqueous medium?   | 02 |
| b.         | What are β-Elimination reactions?  | 01 |
| (xii) a.   | What is Wurtz synthesis?   | 02 |
| b.         | Why all reagents must be dry during the preparation of Grignard's reagent?   | 01 |
| (xiii) a.  | Draw all the possible isomers of C <sub>6</sub> H <sub>13</sub> Cl and classify them as primary, secondary and tertiary                                | 03 |
| (xiv) a.   | How carboxylic acids are obtained from Grignard's reagent?   | 01 |
| b.         | How tertiary alcohols are obtained from R-Mg-X?  | 01 |
| c.         | How tetraethyl lead is obtained from alkyl halides?  | 01 |
| (xv) a.    | What is a carbocation? Write two methods for its generation?   | 02 |
| b.         | How alkyl halides can be prepared from alkanes?  | 01 |
| (xvi) a.   | Write mechanism of E2 reaction.  | 01 |
| b.         | Give two methods to produce primary alcohols from Grignard's reagent.  | 02 |
| (xvii) a.  | Differentiate between E1 and E2 reaction.  | 02 |
| b.         | How may Grignard's reagent may be prepared in laboratory?  | 01 |
| (xviii) a. | Iodide ion is both a good leaving group and a good nucleophile. Explain why?   | 02 |
| b.         | How may PCl <sub>5</sub> be used for the preparation of alkyl halides?   | 01 |
| (xix) a.   | How alkyl halides can be reduced to alkanes?   | 01 |
| b.         | How alkenes may be converted into alkyl halides?   | 01 |
| c.         | What is the effect of nature of alkyl group on the preparation of Grignard's reagent?  | 01 |

### Section - C

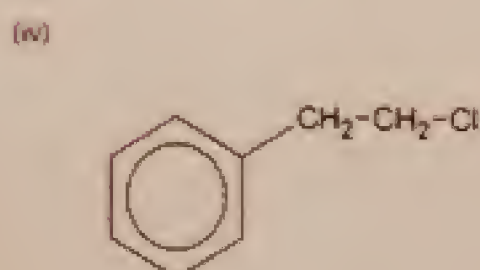
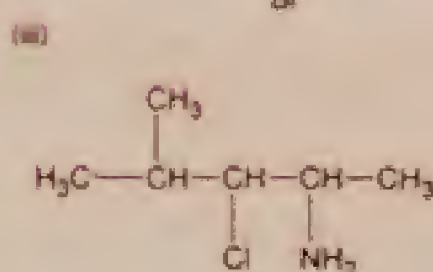
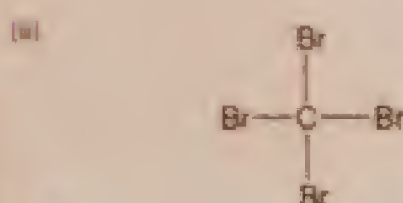
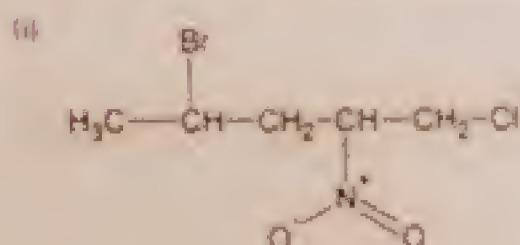
**Note:** Attempt any TWO questions. All questions carry equal marks. (2 × 13 = 26)

- Q. 3. a. Discuss the reactivity of alkyl halides. 04  
b. Discuss classification of alkyl halides. 03  
c. Chloroethene can be obtained from Ethene in the laboratory by the following route:  

$$\text{CH}_2 = \text{CH}_2 \quad (\text{I}) \rightarrow \quad \text{Cl}-\text{CH}_2-\text{CH}_2-\text{Cl} \quad (\text{II}) \rightarrow \quad \text{CH}_2 = \text{CH}-\text{Cl}$$
  
(i) Describe the conditions necessary for each of the reactions I and II. 02  
(ii) Describe the steps in the mechanism of reaction I. 03



- (iii) Name the type of reaction. 01
- Q. 4.** a. Compare in tabular form,  $S_N1$  and  $S_N2$  reactions. 06  
 b. How will you convert ethyl chloride to the  
 (i) Ethyl cyanide (ii) Ethanol (iii) Propane (iv) n-butane (v) Tetraethyl lead 04  
 c. How do tertiary alkyl halide undergo nucleophilic substitution reaction? Give a detailed general mechanism. 03
- Q. 5.** a. Discuss the basicity of amines. 04  
 b. Give the IUPAC names to the following compounds. 04

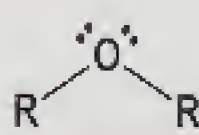
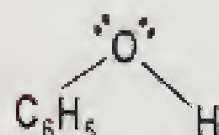
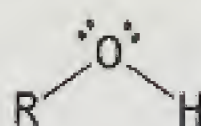
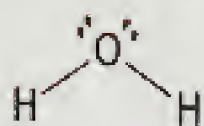


- c. How ethyl magnesium bromide reacts with  
 (i)  $\text{NH}_3$  (ii) Alcohols (iii)  $\text{CO}_2$  (iv) Aldehydes (v) Acetone 05



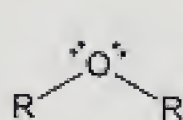
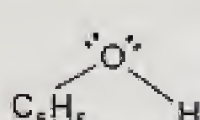
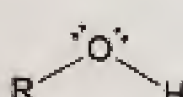
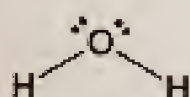
## CHAPTER # 18

# ALCOHOLS, PHENOLS AND ETHERS



## INTRODUCTION

The structure of alcohols, phenols and ethers are much closer to water.



Alcohols and phenols both contain hydroxyl ( $-\text{OH}$ ) group attached to alkyl and phenyl groups, respectively. In ether both hydrogen atoms of water are replaced by alkyl or phenyl groups.

## ALCOHOLS

The aliphatic organic compounds containing hydroxyl group  $-\text{OH}$ , as functional group are called alcohols.

**Monohydric alcohols:** Alcohols containing one  $-\text{OH}$  group are called monohydric alcohols.

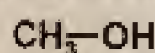
**Polyhydric alcohols:** The alcohols containing two or more hydroxyl groups are known as polyhydric alcohol.

### Classification of Monohydric Alcohols:

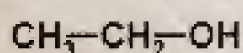
Monohydric alcohols are classified into the following three families:

#### (i) Primary alcohols:

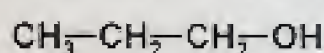
In these, carbon atom attached to  $\text{OH}$  group, is directly attached to one or no carbon atom.



Methanol



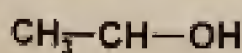
Ethanol



1-Propanol  
(n-propyl alcohol)

#### (ii) Secondary alcohols:

In these, carbon atom attached to  $\text{OH}$  group, is directly attached to two carbon atoms.



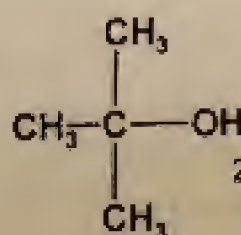
2-Propanol  
(sec-Propyl alcohol)



2-Butanol  
(sec-Butyl alcohol)

#### (iii) Tertiary alcohols:

In these, carbon atom attached to  $\text{OH}$  group, is directly attached to three carbon atoms.



2-Methyl-2-propanol  
(ter-Butyl alcohol)

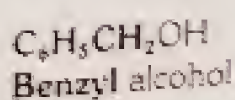
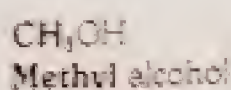


## NOMENCLATURE OF ALCOHOLS:

### 1. Common System of Naming

In common system alcohols are named by adding the word alcohol after the name of the alkyl group to which the  $-OH$  group is attached.

Examples:

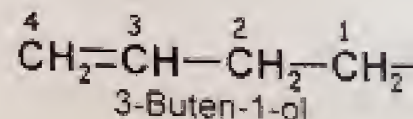
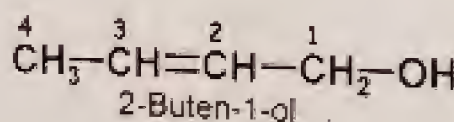
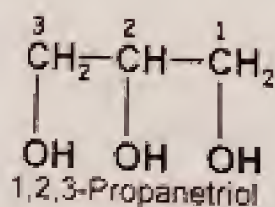
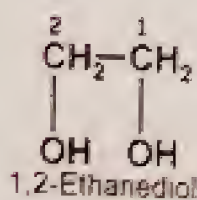
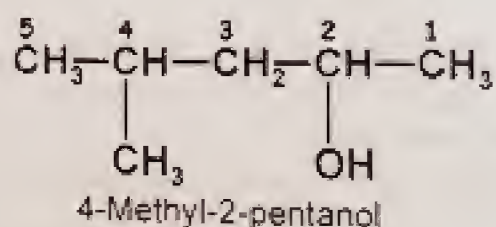
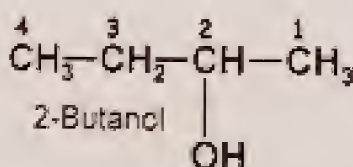
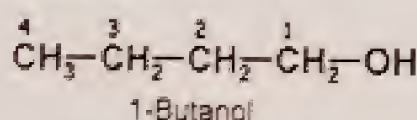


The common names of some alcohols are also given above.

### 2. IUPAC System

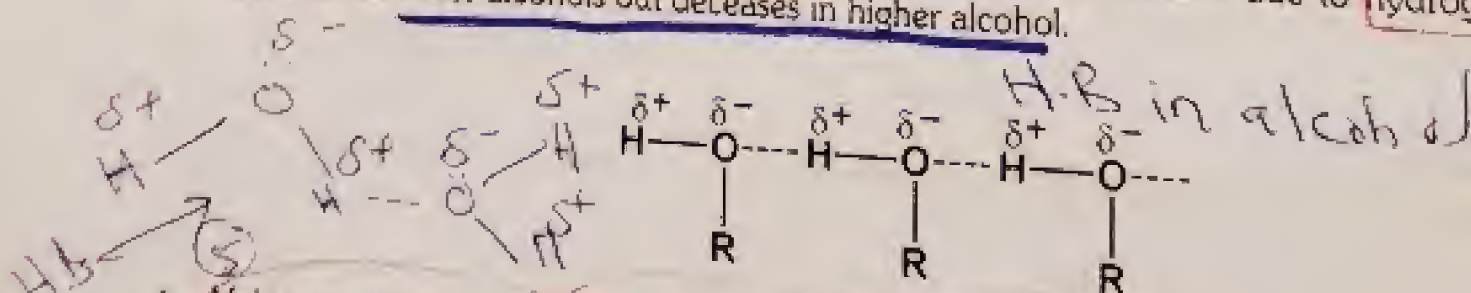
- The longest chain of carbon atoms containing the hydroxyl group is selected as the parent hydrocarbon.
- The ending 'e' of the parent hydrocarbon is replaced by 'ol'.
- The position of  $-OH$  group is indicated by placing the number of carbon to which  $-OH$  is attached before the name of alcohol.
- The carbon chain bearing  $-OH$  group is numbered, beginning from that end which would assign lowest possible number to carbon atom linked to the  $-OH$  group.
- The presence of more than one  $-OH$  groups is indicated by suffixes -diol, -triol, etc. and repeating number of carbon atoms to which  $-OH$  groups are attached.
- In unsaturated alcohol, the hydroxyl group gets the lower number rather than unsaturation, e.g.,

Examples:



### PHYSICAL PROPERTIES:

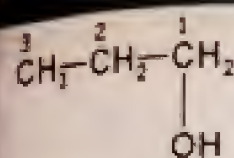
- Alcohol upto butanols are generally colorless liquids. These have characteristic sweet smell and taste. They are readily soluble in water. The solubility of alcohols is due to hydrogen bonding which is significant in lower alcohols but decreases in higher alcohol.



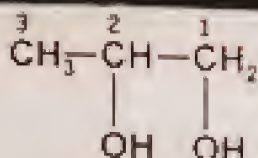
- Melting and boiling points of alcohols are higher than corresponding alkanes. It is due to hydrogen bonding which is present in alcohols but absent in alkanes.



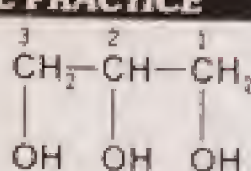
**MORE PRACTICE**



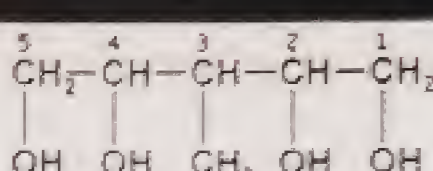
1-Propanol



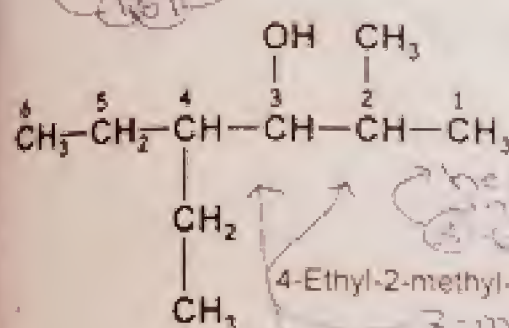
1,2-Propanediol



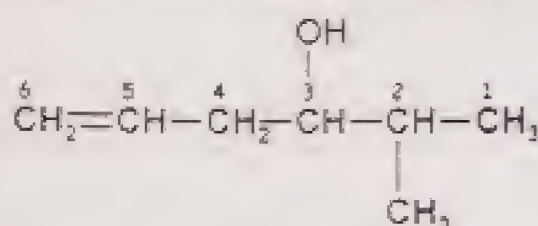
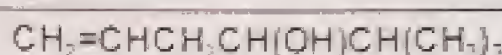
1,2,3-Propanetriol



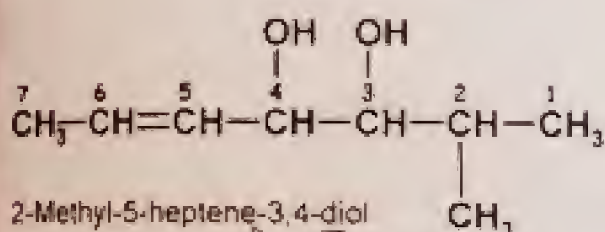
3-Methyl-1,2,4,5-pentanetriol



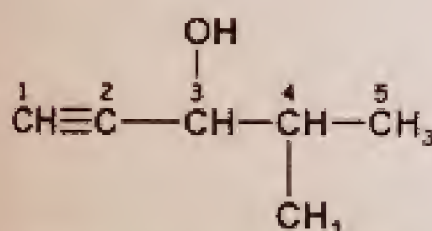
4-Ethyl-2-methyl-3-hexanol



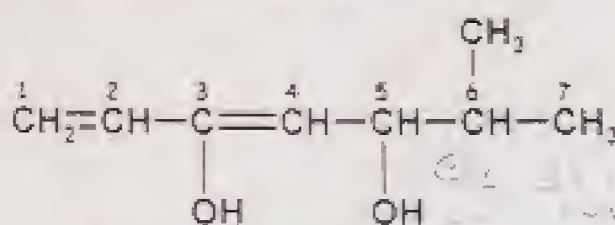
2-Methyl-5-hexen-3-ol



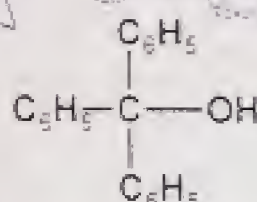
2-Methyl-5-heptene-3,4-diol



4-Methyl-1-pentyn-3-ol



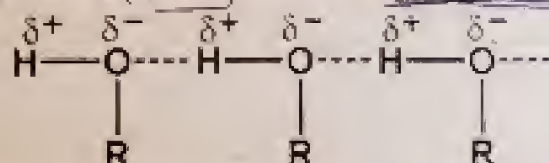
6-Methyl-1,3-heptadiene-3,5-diol



Triphenylmethanol

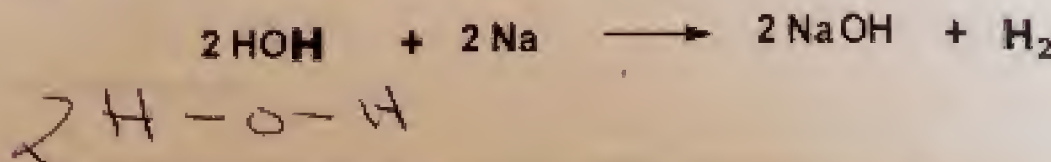
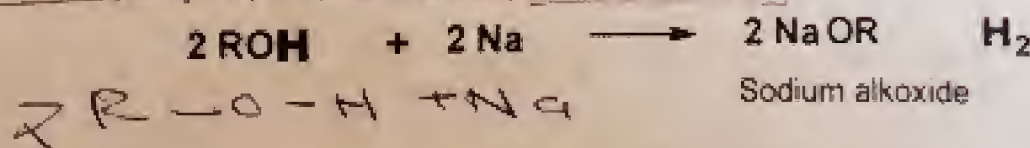
**STRUCTURE:**

- The alcohol functional group consists of an O atom bonded to a C atom and an H atom via  $\sigma$ -bonds.
- Both the C-O and the O-H bonds are polar due to the high electronegativity of the O atom.



**ACIDITY:**

- Due to the electronegativity of the O atoms, alcohols are slightly acidic.
- The anion derived by the deprotonation of an alcohol is the alkoxide ion ( $\text{RO}^-$ ).
- Alkoxides are important bases in organic chemistry.
- Alcohols react with Na (or K) like water to give the alkoxide.



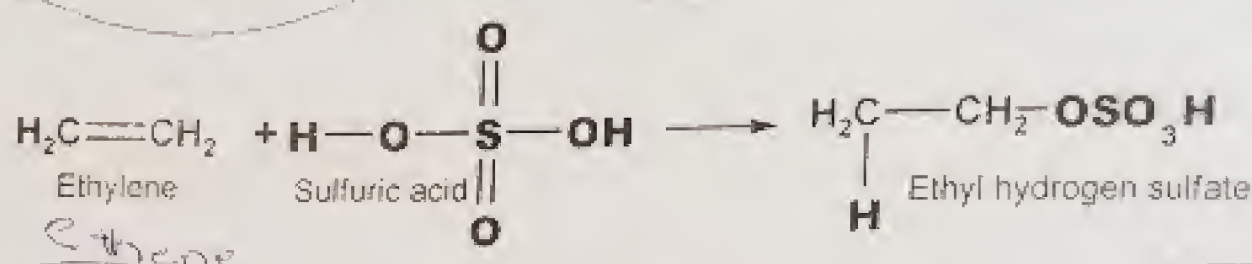


## PREPARATIONS OF ALCOHOLS

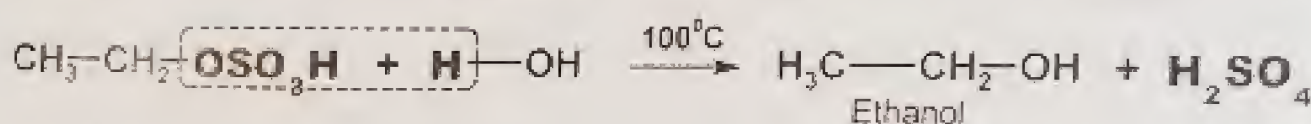
### (1) HYDRATION OF ALKENES

Hydration of alkenes is carried out in the following two steps:

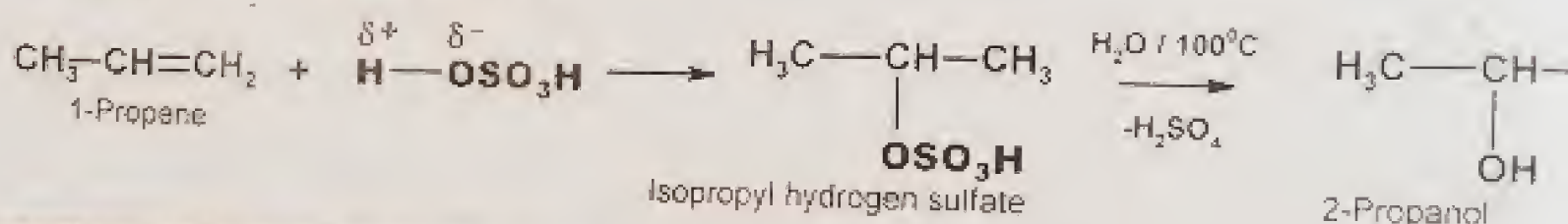
(a) Alkenes are dissolved in concentrated  $H_2SO_4$  to form alkyl hydrogen sulphate



(b) On dilution with water followed by heating alkyl hydrogen sulphates are hydrolyzed to alcohols.

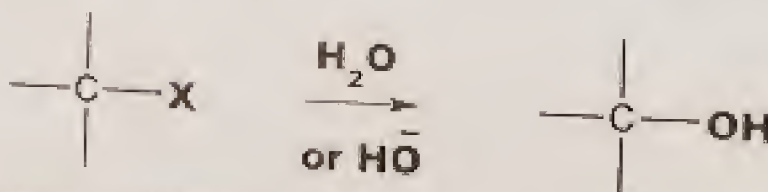


The reaction follows Markownikoff's rule



### (2) HYDROLYSIS OF ALKYL HALIDES

Alkyl halides can be converted to alcohols using water or hydroxide as the nucleophile.



Mechanism is a simple nucleophilic substitution

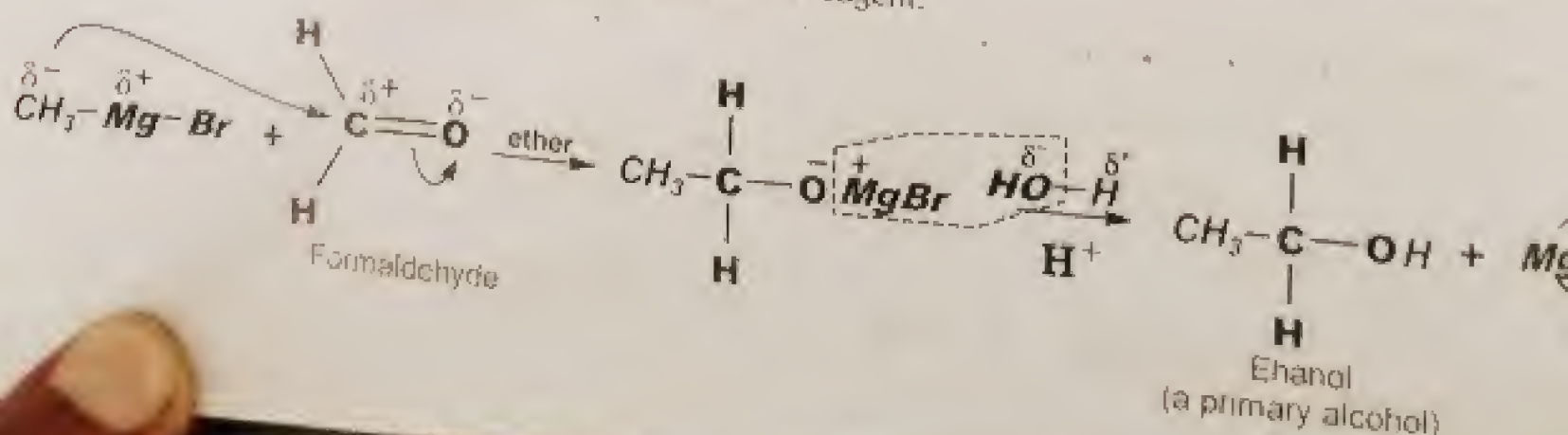
Quick Quiz-1 (5) How Grignard's reagent is used for the preparation of alcohols.

### REACTIONS OF RLi OR RMgX WITH ALDEHYDES AND KETONES

- Primary, secondary and tertiary alcohols can be prepared by the use of Grignard's reagent.
- The Grignard reagent adds to a carbonyl molecule and the resulting compounds forms alcohol on hydrolysis.

(a) Primary alcohol:

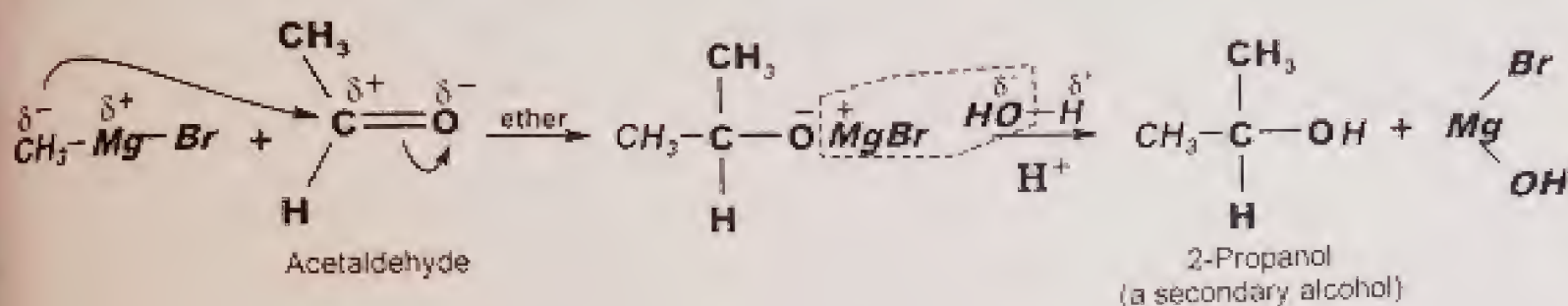
Formaldehyde gives primary alcohol with Grignard's reagent.





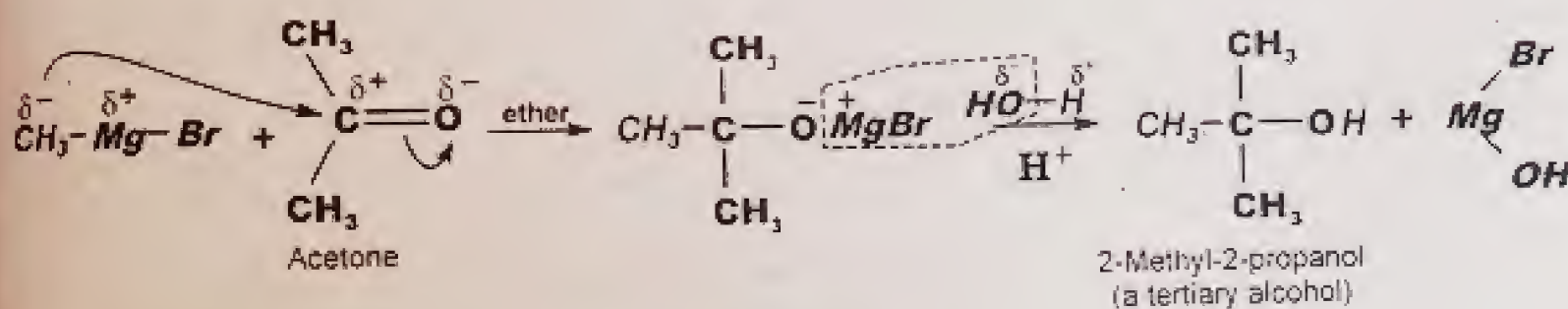
**(b) Secondary Alcohols:**

All aldehydes except formaldehyde give secondary alcohols with Grignard's reagent.



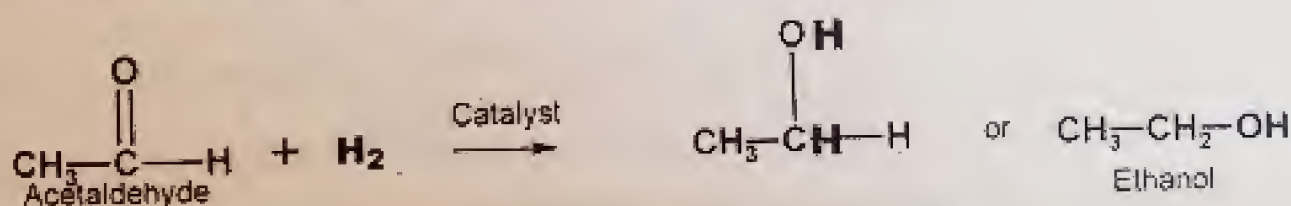
**(c) Tertiary Alcohols:**

Ketones give tertiary alcohols with Grignard's reagent.

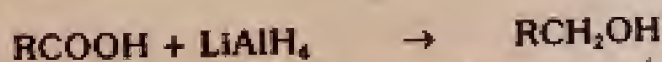


**(4) REDUCTION OF ALDEHYDES AND KETONES**

Reduction of aldehydes, ketones and carboxylic acid (esters in the presence of Ni, Pd or Pt) gives alcohols.

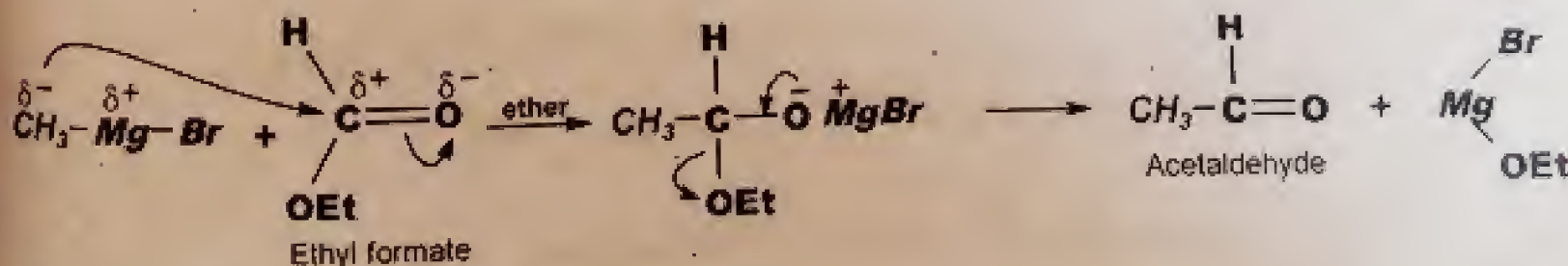


$\text{LiAlH}_4$  can also reduce carboxylic acids as well as aldehydes, ketones and ester.



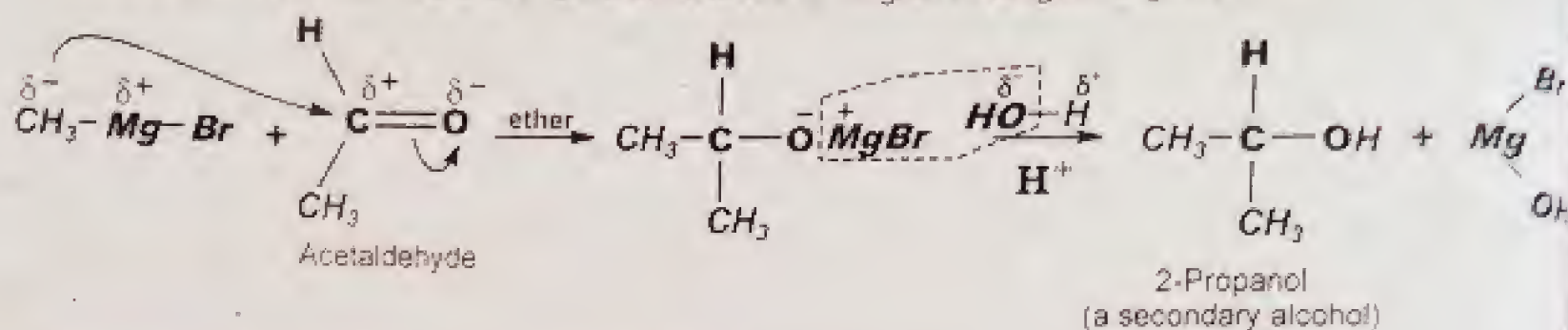
**(5) REACTION OF  $\text{RLi}$  OR  $\text{RMgX}$  WITH ESTERS**

Esters react with Grignard reagents to form alcohols.

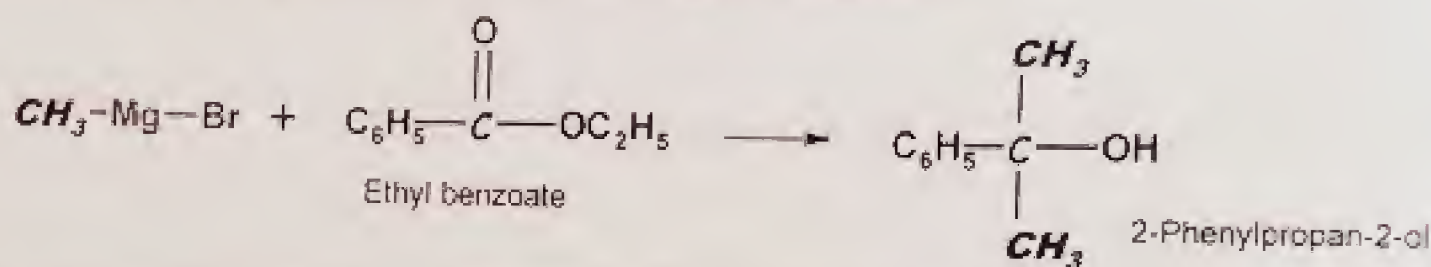




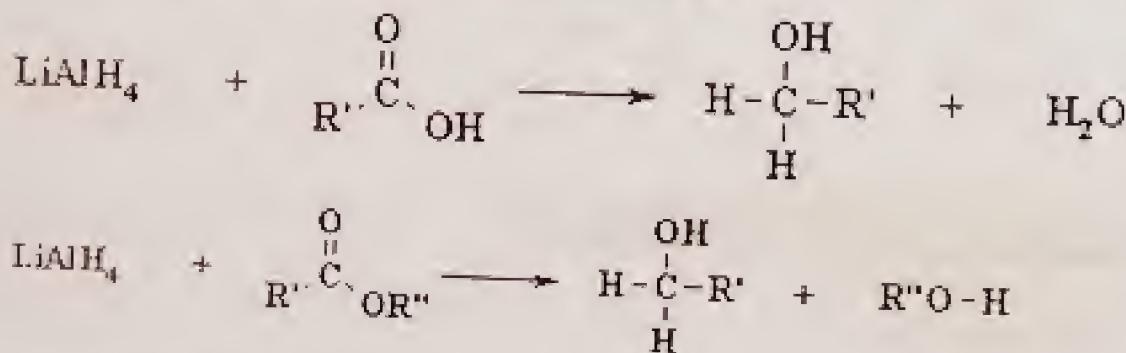
The aldehyde so formed reacts with another molecule of Grignard's reagent to give alcohol.



Similarly other esters give tertiary alcohols with Grignard's Reagents.



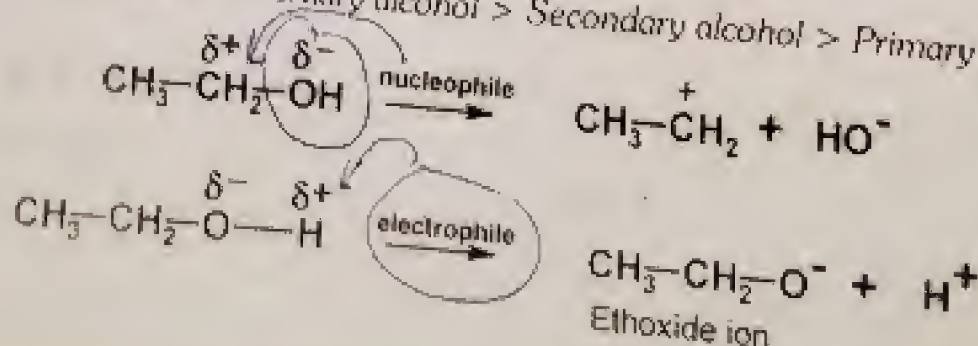
#### (6) REDUCTION OF CARBOXYLIC ACIDS AND ESTERS



- Carboxylic acids and esters are less reactive to **Nucleophiles** than aldehydes or ketones. So, they can only be reduced by  $\text{LiAlH}_4$  and **NOT** by the less reactive  $\text{NaBH}_4$ .
- Each reaction requires that 2 hydrides be added to the carbonyl of acids or esters

#### REACTIVITY:

- Alcohol reacts with other reagents due to the breaking of C-O and O-H bonds.
- Breaking of bonds depends upon the nature of the attacking reagent.
- If a nucleophile attacks, the C-O bond breaks.
- The order of reactivity of alcohols with respect to cleavage of C-O bond is  
 $\text{Tertiary alcohol} > \text{Secondary alcohol} > \text{Primary alcohol}$
- If an electrophile attacks the O-H bond breaks
- The order of reactivity of alcohol with respect to O-H bonds cleavage:  
 $\text{CH}_3\text{OH} > \text{Tertiary alcohol} > \text{Secondary alcohol} > \text{Primary alcohol}$

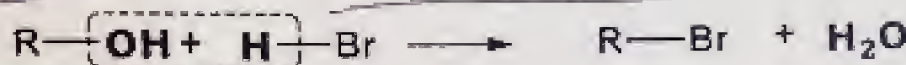




# REACTIONS OF ALCOHOLS

## (1) REACTION WITH HX

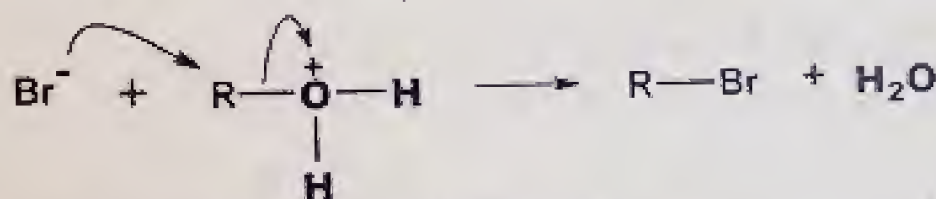
- Due to the presence of unshared electron pairs on the oxygen atom of alcohols, they act as bases and react with halogen acids to form their respective alkyl halides.



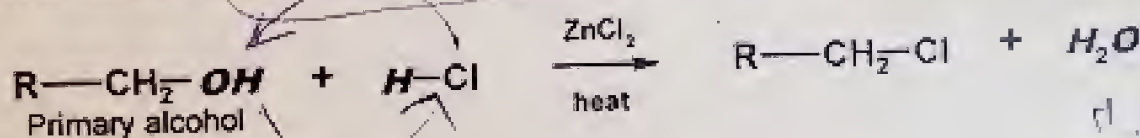
- The C-O bond in an alcohol is very slightly polarized. Therefore the following reaction mechanism is not possible.



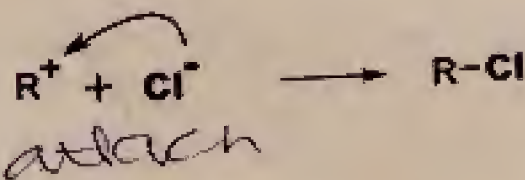
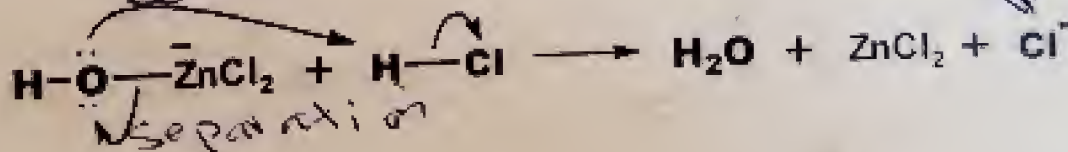
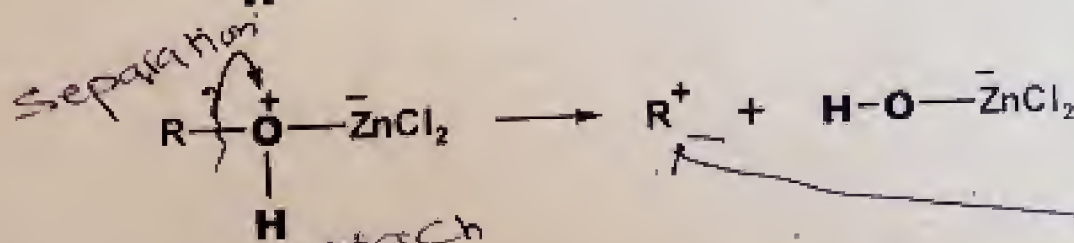
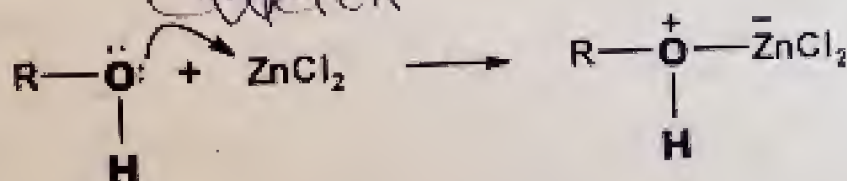
- In fact, the alcohol first acts as a base. It accepts proton from HX to an alkyl oxonium ion. Now the C-O bond becomes highly polarized. Thus, the electrophilic carbon is easily attached by a nucleophile to break C-O bond.



- The orders of reactivity of halogen acids  $\text{HI} > \text{HBr} > \text{HCl}$
- The orders of reactivity of alcohols is  $\text{ter-alcohol} > \text{sec-alcohol} > \text{prim-alcohol}$ .
- HCl and prim-alcohol are the least reactive amongst halogen acids and alcohols respectively. Therefore they react only in the presence of a catalyst. A solution of  $\text{ZnCl}_2$  in concentrated HCl is used as a catalyst.



### Mechanism



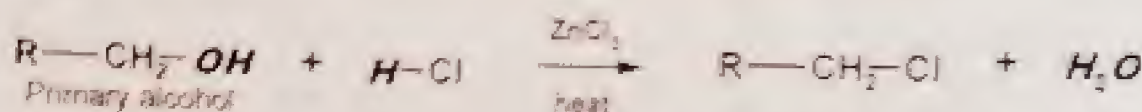


**Exercise Q3** How will you distinguish between primary, secondary and tertiary alcohols? Explain reactions.

**LUCAS TEST:**

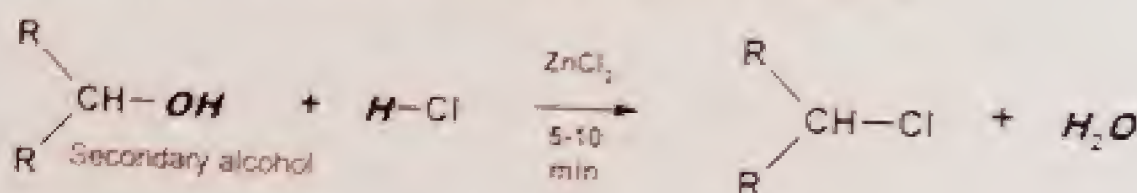
- The difference of chemical reactivity of alcohols with halogen acids is used for their identification.
- For identification purpose, the alcohol is treated with a solution of  $ZnCl_2$  in concentrated  $HCl$ . This reagent is called Lucas reagent.

(i) Tertiary alcohol immediately forms an insoluble layer of a ter-alkyl chloride.

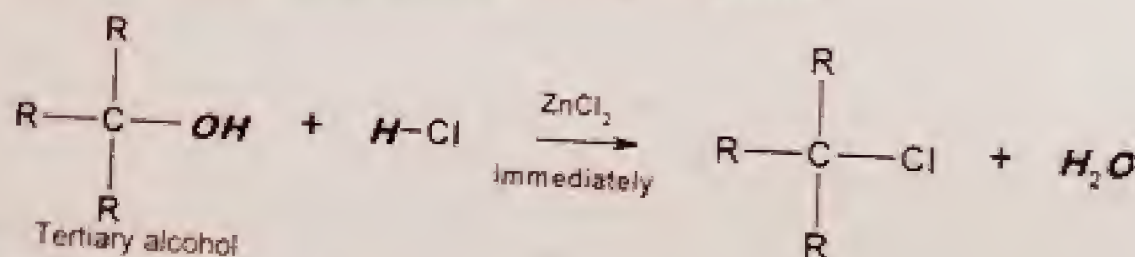


20 - 25 min

(ii) Secondary alcohol forms an insoluble sec-alkyl chloride in 5-10 minutes.



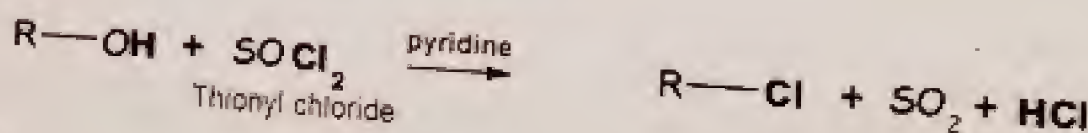
(iii) Primary alcohol forms an insoluble prim-alkyl chloride on heating.



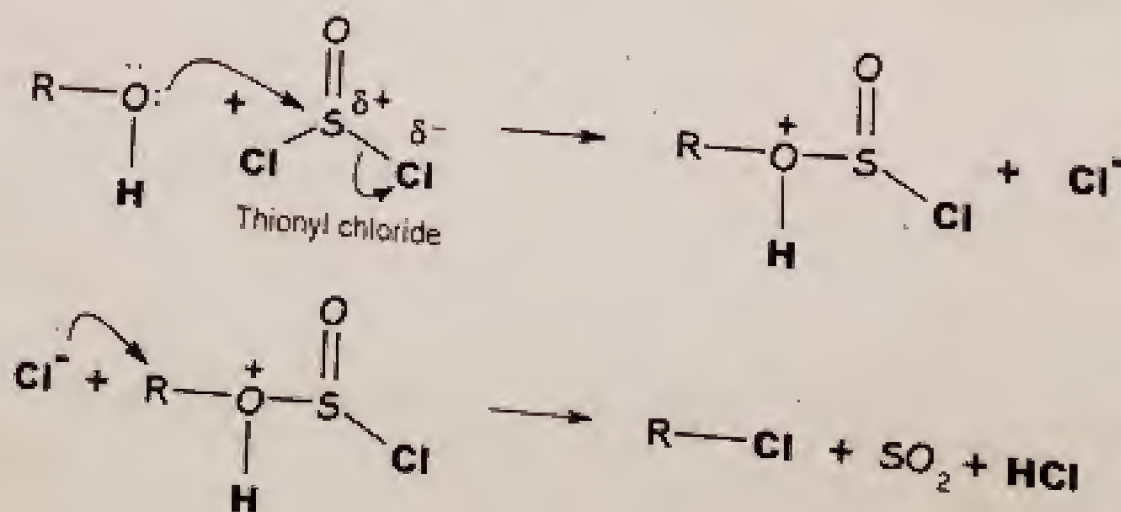
**(2) REACTION WITH  $SOCl_2$ ,  $PX$**

(i) **Thionylchloride ( $SOCl_2$ )**

Alcohols react with thionylchloride to give alkyl chlorides.



**Mechanism**





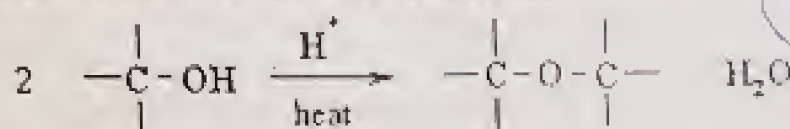
(iii) **Phosphorus Tribromide and Triiodide ( $PBr_3$  and  $PI_3$ )**

Alkyl bromides and iodides are best prepared by treating alcohols with  $PBr_3$  and  $PI_3$ .



(3) **ACID CATALYZED DEHYDRATION**

Ethers are produced via acid-catalyzed dehydration of alcohols

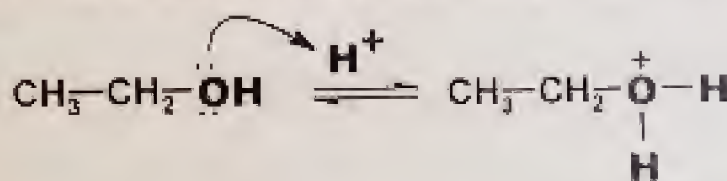


- Reagents are typically  $H_2SO_4$  and heat.
- This method is limited to **symmetrical** ethers of **primary** alcohols.
- The method is not suitable for unsymmetrical ethers.

**MECHANISM**

**Step 1:**

The lone pairs on the oxygen make it a Lewis base. So first step is an acid/base reaction. The alcoholic oxygen is protonated to make a better leaving group (i.e.  $H_2O$ ). This step is very fast and reversible.



**Step 2:**

The O of the second alcohol molecule functions as the nucleophile. It attacks and displaces the good leaving group ( $H_2O$ ) by breaking the C-O bond. This forms an oxonium ion intermediate.



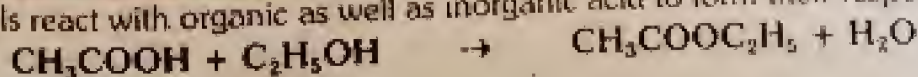
**Step 3:**

This is another acid / base reaction. The proton is removed by a suitable base. In this reaction water molecule removes the proton. The alcohol ROH can also do this. Thus, the ether product is formed.

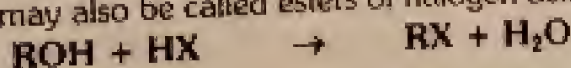


(4) **PREPARATION OF ESTERS**

- Alcohols react with organic as well as inorganic acid to form their respective esters.

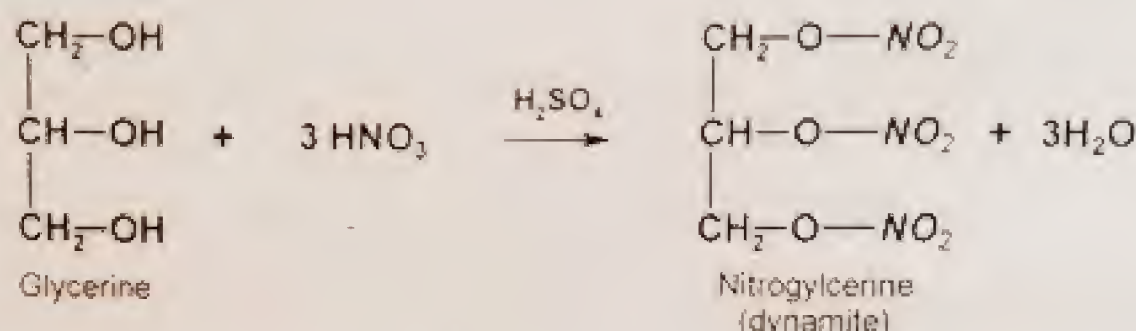


- Thus alkyl halides may also be called esters of halogen acids.

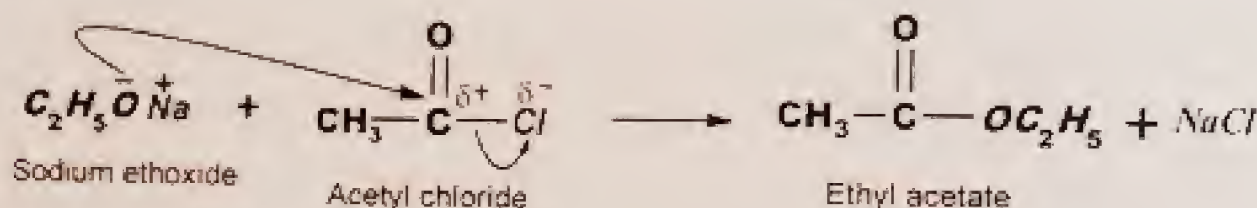




- Glycerine reacts with a mixture of concentrated  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  to give an ester called Nitroglycerine or Glycerylnitrate



- Nitroglycerine is highly explosive liquid. It is mixed with fine sand and moulded into sticks called Dynamite.
- Esters are also formed by treating acid chlorides with sodium alkoxides.

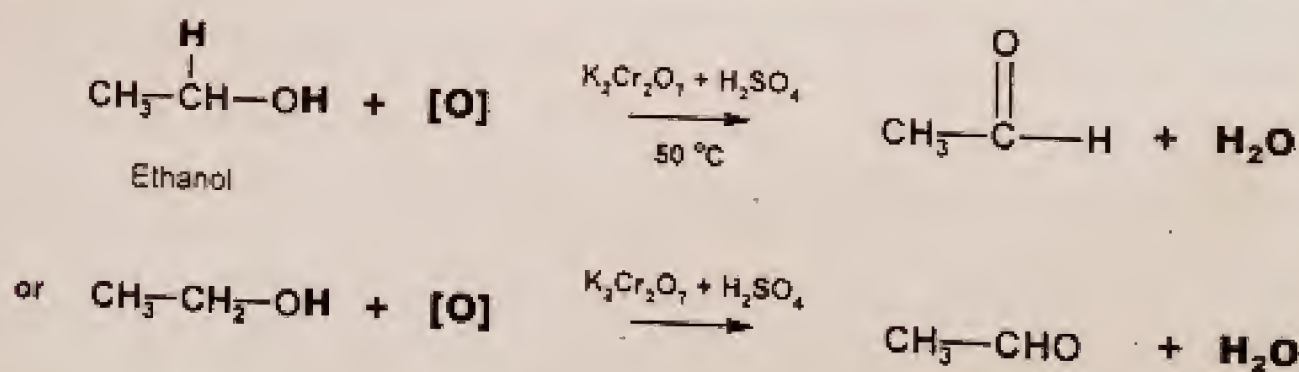


### (5) OXIDATION

Alcohols are easily oxidized by alkaline  $\text{KMnO}_4$  or  $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$  solutions to give different products.

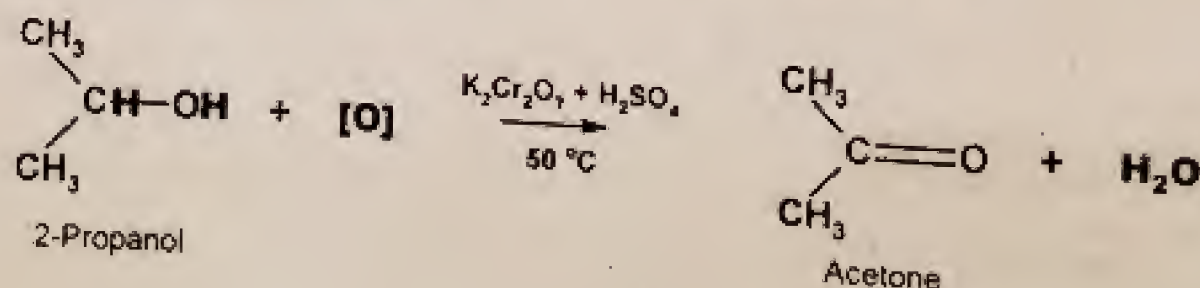
#### (i) Primary Alcohol:

A primary alcohol is first oxidized to an aldehyde, which is further oxidized to a carboxylic acid.



#### (ii) Secondary Alcohol

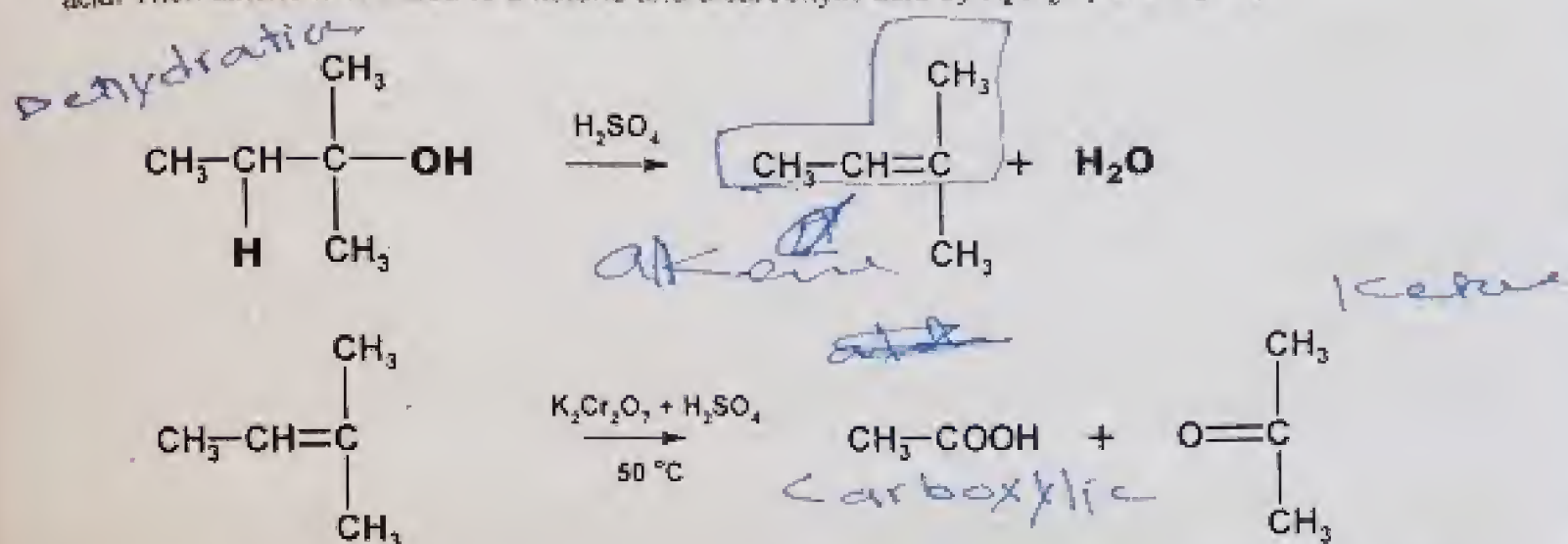
A secondary alcohol is oxidized to give a ketone which is not further oxidized.





**(III) Tertiary Alcohol:**

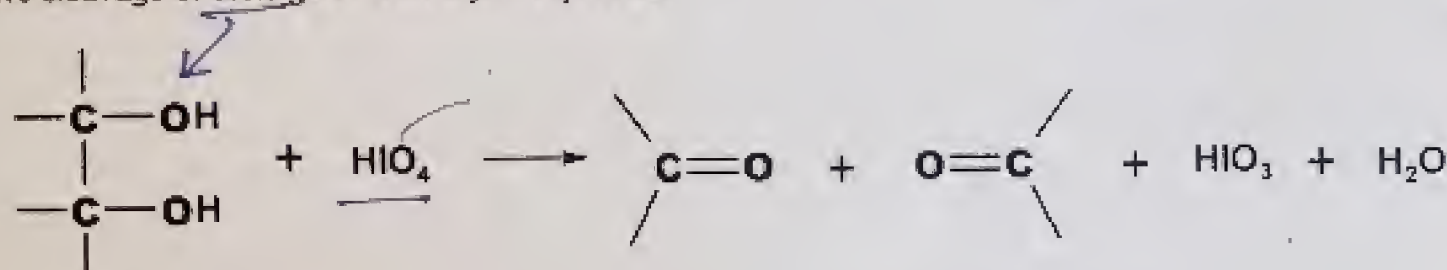
- A tertiary alcohol is not oxidized by alkaline  $\text{KMnO}_4$ .
- When heated with a mixture of  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$ , it is first dehydrated to an alkene in the presence of acid. Then alkene is oxidized to a ketone and a carboxylic acid by  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{SO}_4$ .



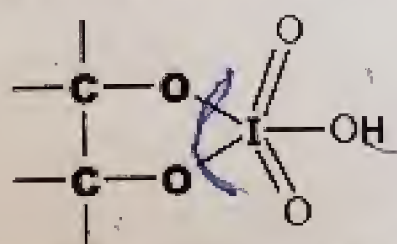
- Thus, each of the products contains lesser number of carbon atoms than the parent alcohol molecule.

**(6) CLEAVAGE OF 1,2-DIOLS**

Oxidative cleavage of diols gives carbonyl compounds.



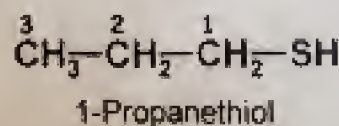
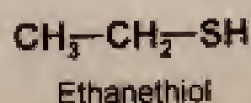
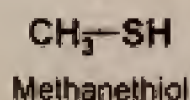
- 1,2- or vicinal diols are cleaved by periodic acid,  $\text{HIO}_4$ , into two carbonyl compounds.
- The reaction is selective for 1,2-diols.
- This can be used as a functional group test for 1,2-diols.
- The products are determined by the substituents on the diol.
- The reaction occurs via the formation of a cyclic periodate ester.



**THE SULFUR ANALOGUES (THIOLS,  $\text{RSH}$ )**

**NOMENCLATURE**

- Thiols are the sulfur analogues of alcohols.
- These are named by adding the suffix **-thiol** to the name of corresponding alkanes.



- The rest of nomenclature (i.e. naming substituents etc.) is similar to alcohols



## PHYSICAL PROPERTIES

- Hydrogen bonding is much weaker than that in alcohols.
- Lower boiling points than similar alcohols.

## STRUCTURE

- The thiol functional group consists of an **S** atom bonded to a **C** atom and a **H** atom via  $\sigma$ -bonds.
- Generally, the structure is similar to alcohols. However, bonds to **S** are longer and weaker than those to **O**.
- The **S-H** bonds is less polar than that in alcohols since **S** is less electronegative than **O**.

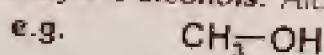
## REACTIVITY

- Thiols are much more acidic than similar alcohols, e.g.  $\text{RSH}$  ( $\text{pK}_a = 10$ ) versus  $\text{ROH}$  ( $\text{pK}_a = 16$  to  $19$ ).
- Thiols are also much more nucleophilic than similar alcohols, in fact  $\text{RSH}$  is about as nucleophilic as  $\text{RO}^-$ .
- Thiols are readily oxidized but to **S-O** systems rather than **C=S** systems.
- Thiols are commonly oxidized to disulfides, **R-S-S-R**, a biologically important reaction.

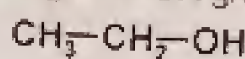
## QUICK QUIZ-1

(1) What are monohydric and polyhydric alcohols?

**Monohydric alcohols:** Alcohols containing one  $-\text{OH}$  group are called monohydric alcohols.

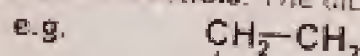


Methanol

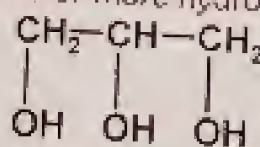


Ethanol

**Polyhydric alcohols:** The alcohols containing two or more hydroxyl groups are known as polyhydric alcohols.



1,2-Ethanediol

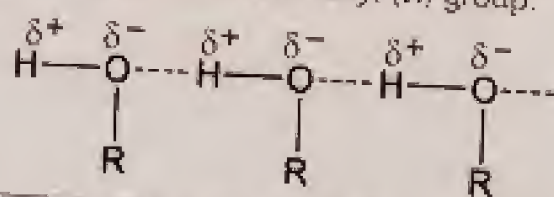


1,2,3-Propanetriol

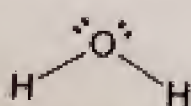
(2) Why some alcohols are readily soluble in water

Small alcohols, e.g. methanol and ethanol, are readily soluble in water.

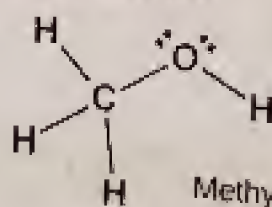
The solubility of alcohols is due to hydrogen bonding which is significant in lower alcohols but decreases in higher alcohol due to increase in non-polar nature of alkyl (R) group.



(3) Write the structures of water and methyl alcohol.



Water



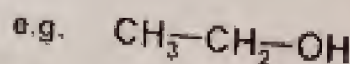
Methyl alcohol

(4) Write the formulas of primary, secondary and tertiary alcohols.

**Primary alcohols:** In these, carbon atom attached to  $\text{OH}$  group, is directly attached to one or no carbon atom.



Primary alcohol



Ethanol

(5) How Grignard's reagent is used for the preparation of alcohols.



(6) Define deprotonation

The removal of a proton ( $H^+$ ) from molecule, or an ion, forming its conjugate base is called deprotonation.



The alkoxide ion ( $RO^-$ ) is the conjugate base of alcohol ( $ROH$ )

(7) What is a reagent?

A reagent is a compound or a mixture that is added to a system to cause a chemical reaction or test if a reaction occurs

e.g. Baeyer's reagent is dilute solution of  $KMnO_4$ . It is used to test the presence of a double bond. It reacts with a double bond to form a glycol.

## PHENOLS

### INTRODUCTION

Aromatic compounds containing one or more OH groups, directly attached with carbon of benzene ring, are called phenols.

- The simplest example phenol is also known as carbolic acid, i.e.,  $C_6H_5OH$ . It was first obtained from coal tar by Runge in 1834.
- Phenol is derived from the old name for benzene (**phene**), and a suffix (**ol**) is added to it that indicates the presence of hydroxyl group.
- Brief information about phenol.

First prepared by Runge: Melting point =  $41^\circ C$ ; Boiling point =  $182^\circ C$ ;

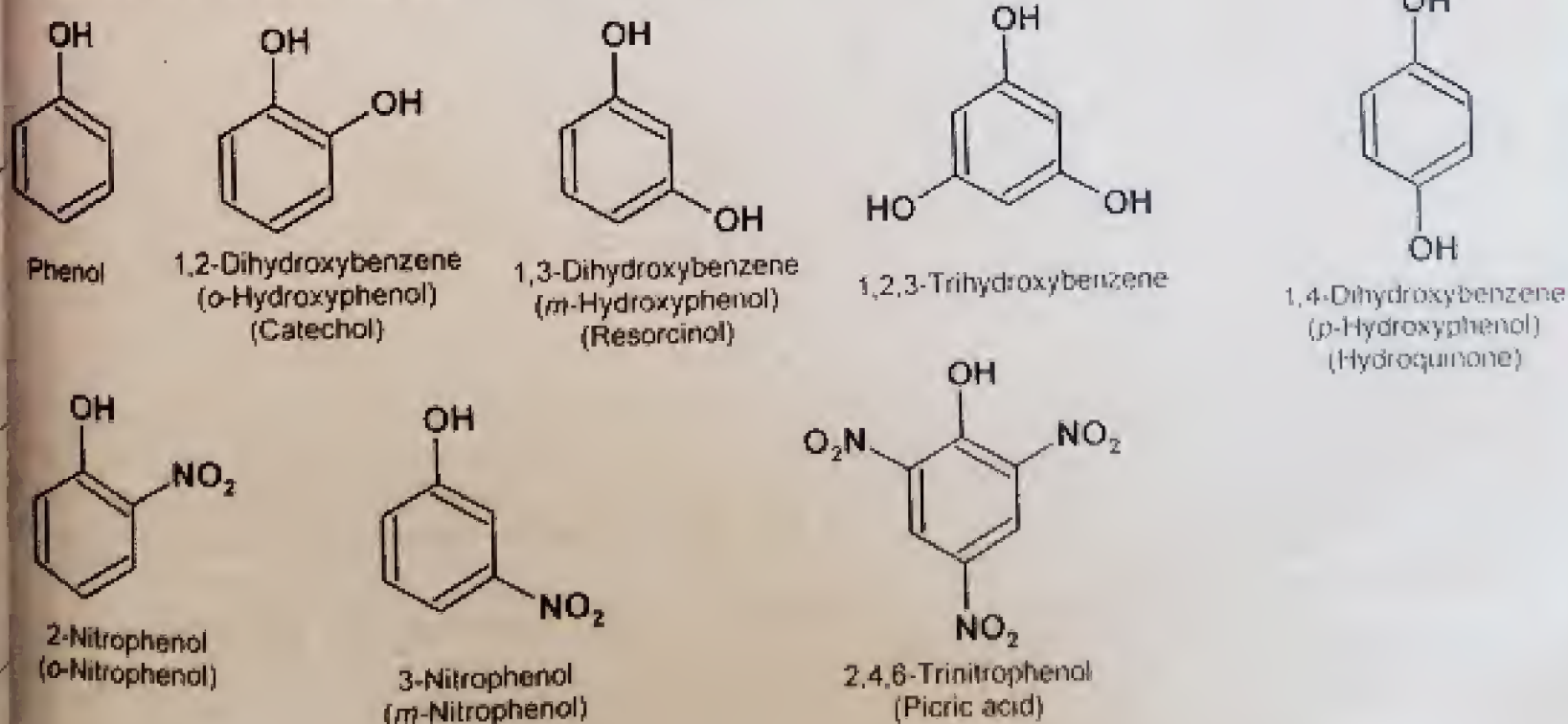
Simplest example of phenol is Carbolic acid ( $C_6H_5OH$ )

- Phenols can be obtained via **substitution** reactions, with the hydrolysis of diazonium salts being the most important laboratory method.
- Phenols are acidic and are important intermediates in the preparation of aryl ethers,  $C_6H_5-OR$

**NOTE:** The word **phenol** ( $C_6H_5-OH$ ) is often confused with **phenyl** ( $C_6H_5-$ ).

### NOMENCLATURE

In common system alcohols are named by adding the word 'alcohol' after the name of the alkyl group to which the  $-OH$  group is attached.





### STRUCTURE

- The alcohol functional group consists of an O atom bonded to an  $sp^2$ -hybridized aromatic C atom and H atom via  $\sigma$ -bonds.
- Both the C-O and the O-H bonds are polar due to the high electronegativity of the O atom.
- Conjugation exists between an unshared electron pair on the oxygen and the aromatic ring. Hence as compare to simple alcohols, the phenol shows following properties
  - a shorter carbon-oxygen bond distance
  - a more basic hydroxyl oxygen
  - a more acidic hydroxyl proton (-OH)

### PHYSICAL PROPERTIES:

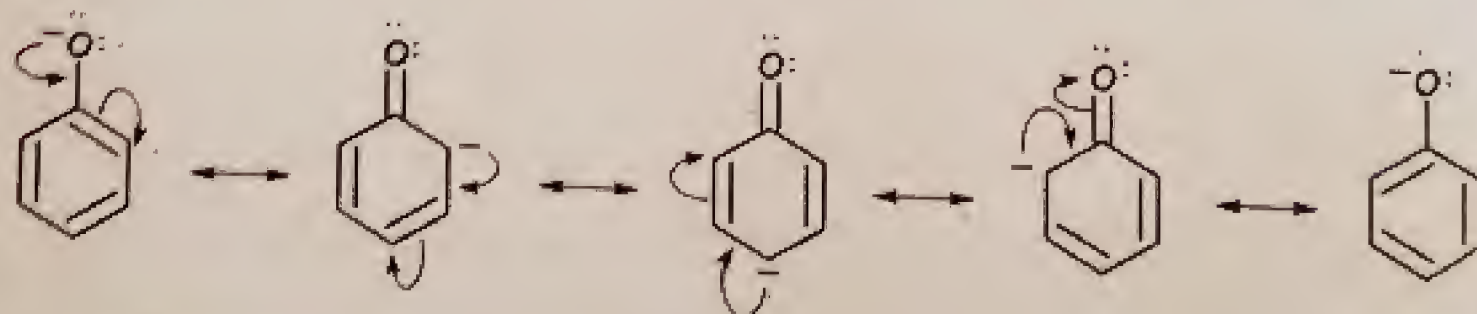
- Phenol is a colorless, crystalline, poisonous solid with characteristic phenolic odor having melting point  $41^\circ\text{C}$  and boiling point  $182^\circ\text{C}$ .
- It is sparingly soluble in water forming pink solution at room temperature but completely soluble above  $68.5^\circ\text{C}$ .
- It is poisonous and causes blisters on the skin.

### ACIDITY:

- Phenols are more acidic ( $pK_a \approx 10$ ) than alcohols ( $pK_a \approx 16 - 20$ ), but less acidic than carboxylic acids ( $pK_a \approx 5$ ).
- Phenol ionizes in water as



- The negative charge of the phenolate ion is stabilized by resonance due to electron delocalization in the benzene ring as shown below:



- The acidity difference means that it is possible to separate phenols from alcohols and/or carboxylic acids. When an ether solution, of either phenol and alcohol or phenol and carboxylic acid is mixed with dilute base (sodium hydroxide and sodium bicarbonate, respectively) then the stronger acid is converted into its alkali salt. This salt is extracted to the aqueous phase and can be separated from the organic phase.
- Nucleophilic substitution reactions of phenols are generally carried out under basic conditions as the phenolate ion is a better nucleophile.



### SUBSTITUENT EFFECTS ON ACIDITY

- Substituents can greatly influence the acidity of the phenol due to resonance and / or inductive effects. The groups located ortho or para to the -OH group greatly influence the acidity.
- Electron withdrawing groups enhance the acidity.
- Electron donating substituents decrease the acidity.
- e.g. The resonance stabilization of o-nitrophenol is shown below:

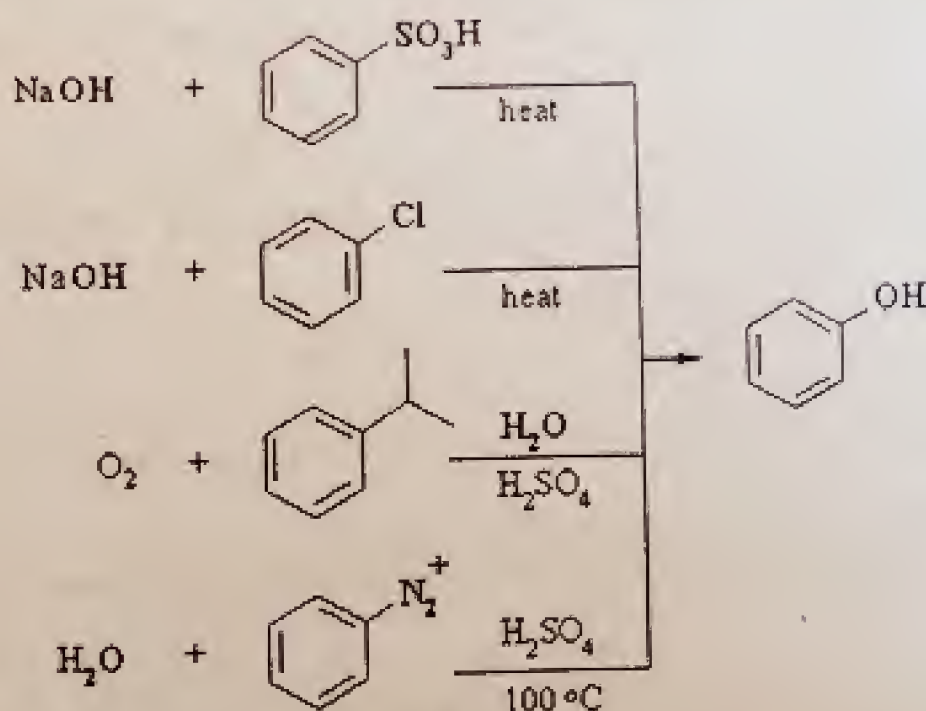


Carbonyl group

Compound	pKa	Compound	pKa
Phenol	10.0		
o-Methoxyphenol	10.0	p-Methoxyphenol	10.2
o-Methylphenol	10.3	p-Methylphenol	10.3
o-Chlorophenol	8.6	p-Chlorophenol	9.4

### PREPARATIONS OF PHENOLS

Summary:



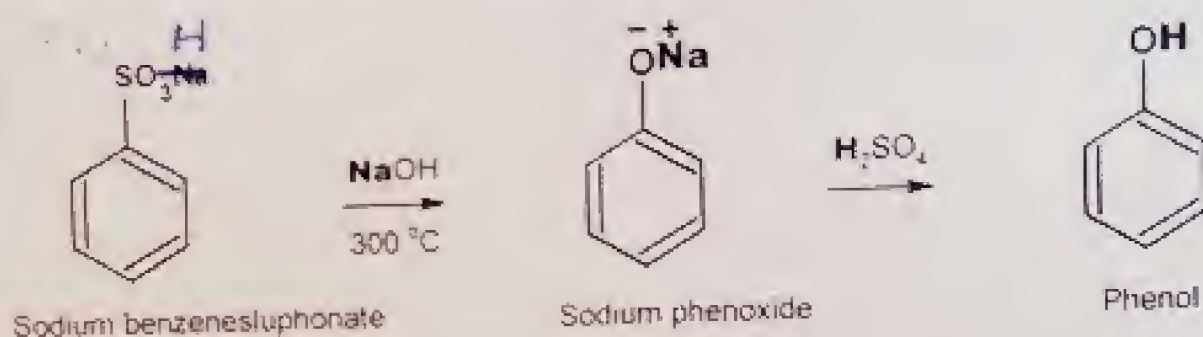
NOTE:

- The first three methods are primarily industrial methods.
- The hydrolysis of diazonium salts is the most important laboratory method.



### 1. REACTION OF BENZENE SULFONIC ACID WITH HYDROXIDE

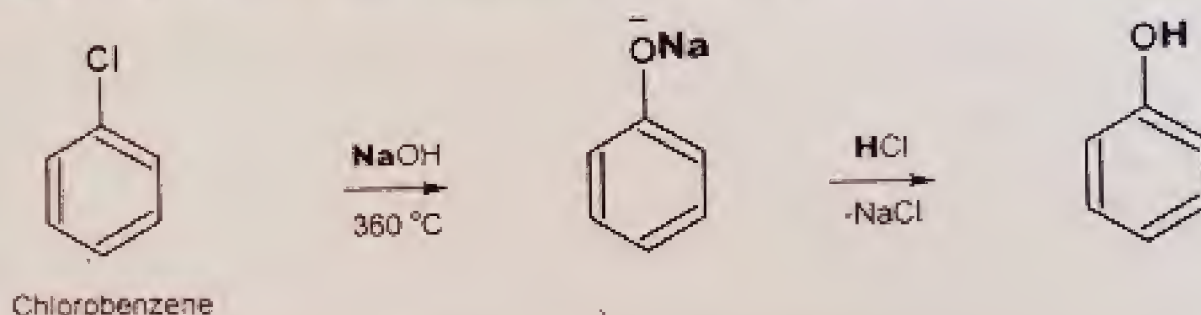
Sodium benzenesulphonate on fusion with strong alkali like NaOH or KOH, yields phenol.



- At such a high temperature, side reactions also occur.

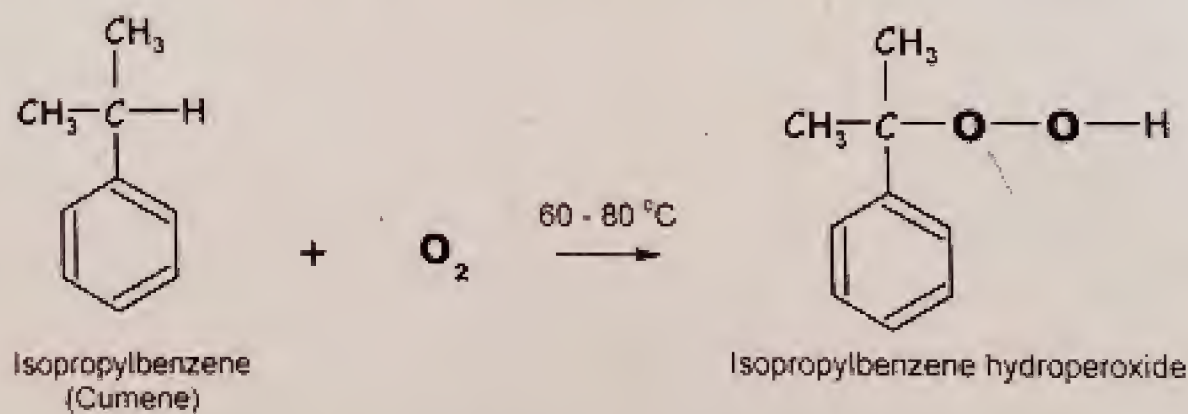
### 2) BASE HYDROLYSIS OF CHLOROBENZENE

Chlorobenzene is hydrolyzed by heating with NaOH at 360°C and under high pressure.

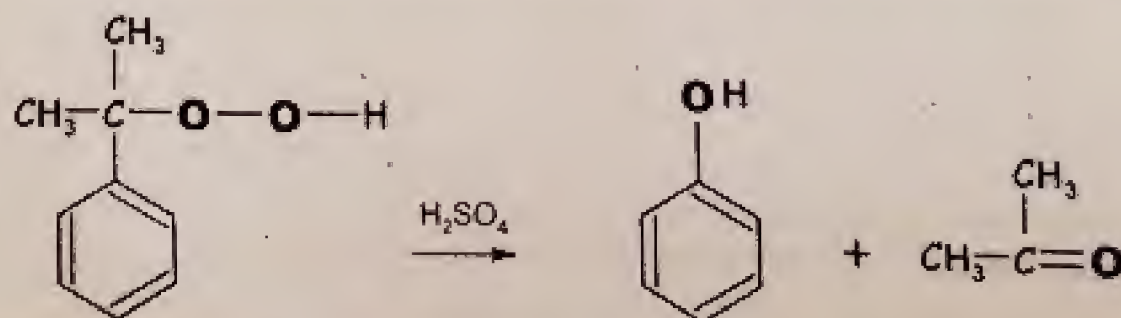


### 3) ACIDIC OXIDATION OF CUMENE

- It is recently developed commercial method for the preparation of phenol.
- Cumene is oxidized by atmospheric oxygen in presence of metal catalyst, into cumene hydroperoxide.



- The hydroperoxide is converted into phenol through an acid catalyzed rearrangement.





#### (4) PREPARATION OF PHENOLS FROM ARYL DIAZONIUM SALTS



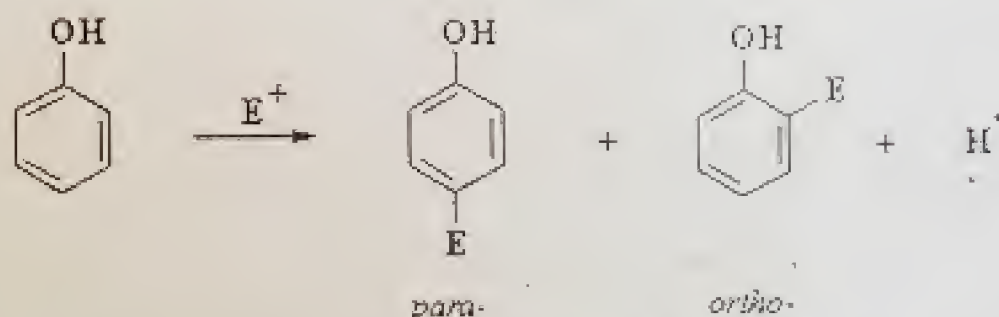
- Aryl diazonium salts can be converted into phenols using  $\text{H}_2\text{O} / \text{H}_2\text{SO}_4$  / heat
- Aryl diazonium salts are prepared by reaction of aryl amines with nitrous acid,  $\text{HNO}_2$

#### REACTIVITY:

- Phenols are very reactive towards electrophilic aromatic substitution
- The OH group is an ortho- / para- director therefore it produces ortho- / para- products
- The OH group is an electron donating group and it donates electrons to the benzene ring. Thus, it activates the ring. Hence, mild conditions are needed for phenol than that for benzene.

#### REACTIONS OF PHENOLS

- Phenols are very reactive towards electrophilic aromatic substitution.
- It is because the hydroxy group, -OH, is a strongly activating, ortho- / para- directing substituent.



- Substitution typically occurs para to the hydroxyl group. If the para position is blocked, then ortho substitution occurs.
- The strong activation by OH group means that milder reaction conditions can be used than those used for benzene.
- Phenols are so activated that polysubstitution can occur. The polysubstitution is a problem.

Reaction	Phenol	Benzene
Nitration	dil. $\text{HNO}_3$ in $\text{H}_2\text{O}$ or $\text{CH}_3\text{CO}_2\text{H}$	$\text{HNO}_3 / \text{H}_2\text{SO}_4$
Sulfonation	conc. $\text{H}_2\text{SO}_4$	$\text{H}_2\text{SO}_4$ or $\text{SO}_3 / \text{H}_2\text{SO}_4$
Halogenation	$\text{X}_2$	$\text{X}_2 / \text{Fe}$ or $\text{FeX}_3$
Alkylation	$\text{ROH} / \text{H}^+$ or $\text{RCI} / \text{AlCl}_3$	$\text{RCI} / \text{AlCl}_3$
Acylation	$\text{RCOI} / \text{AlCl}_3$	$\text{RCOI} / \text{AlCl}_3$
Nitrosation	aq. $\text{NaNO}_2 / \text{H}^+$	

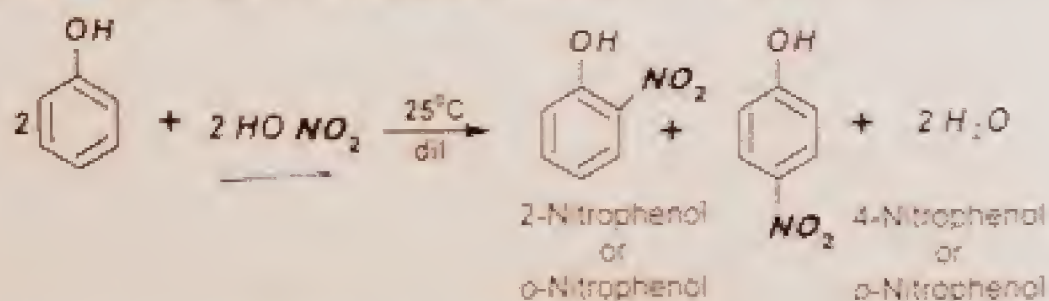
Some of these reactions are given on next page



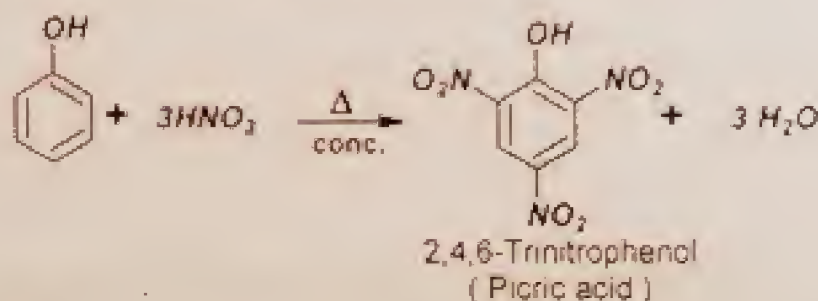
## SOME USEFUL ELECTROPHILIC SUBSTITUTION REACTIONS OF PHENOL

### NITRATION

Phenol reacts with dil.  $\text{HNO}_3$  to give a mixture of *o*- and *p*-nitrophenols

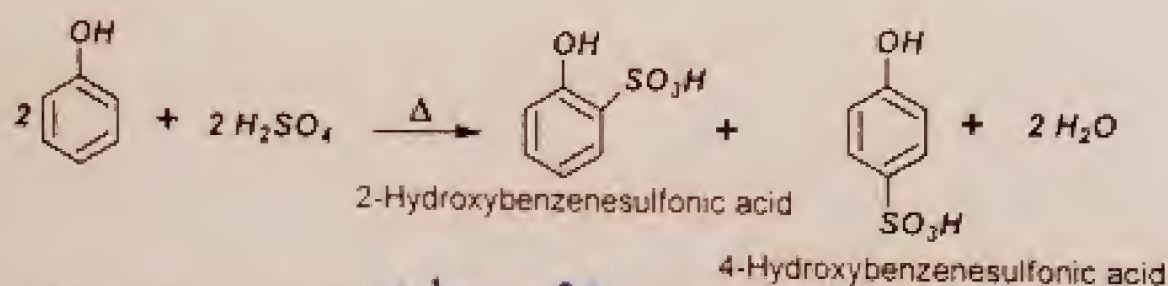


Phenol reacts with conc.  $\text{HNO}_3$  to give picric acid



### SULPHONATION

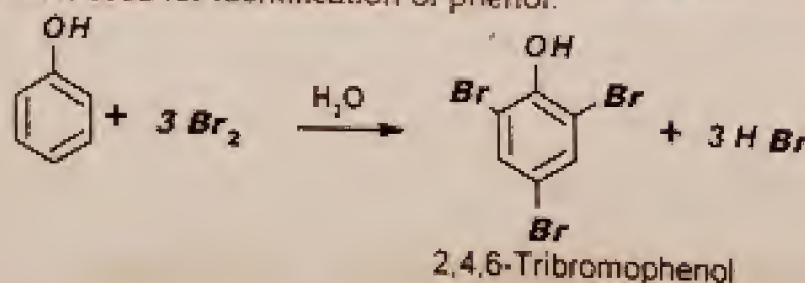
- Phenol reacts with conc.  $\text{H}_2\text{SO}_4$  at room temperature to give *o*- and *p*-hydroxybenzenesulphonic acids.
- At  $20^\circ\text{C}$  *o*-isomer is formed in greater percentage, while at  $100^\circ\text{C}$ , *p*-isomer is formed in greater percentage.



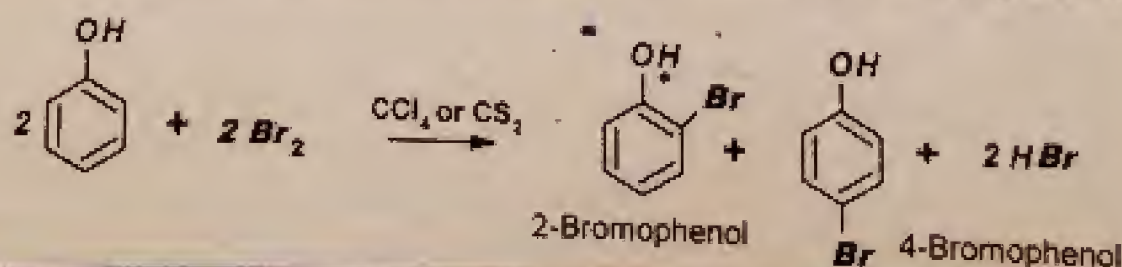
### HALOGENATION

*No Alcohol gives*

- Aqueous solution of phenol reacts with bromine water to give white precipitates of 2,4,6-tribromophenol. This test is used for identification of phenol.



- When  $\text{Br}_2$  is reacted in anhydrous solvent like  $\text{CS}_2$ , a mixture of *o*- and *p*-bromophenol is produced.



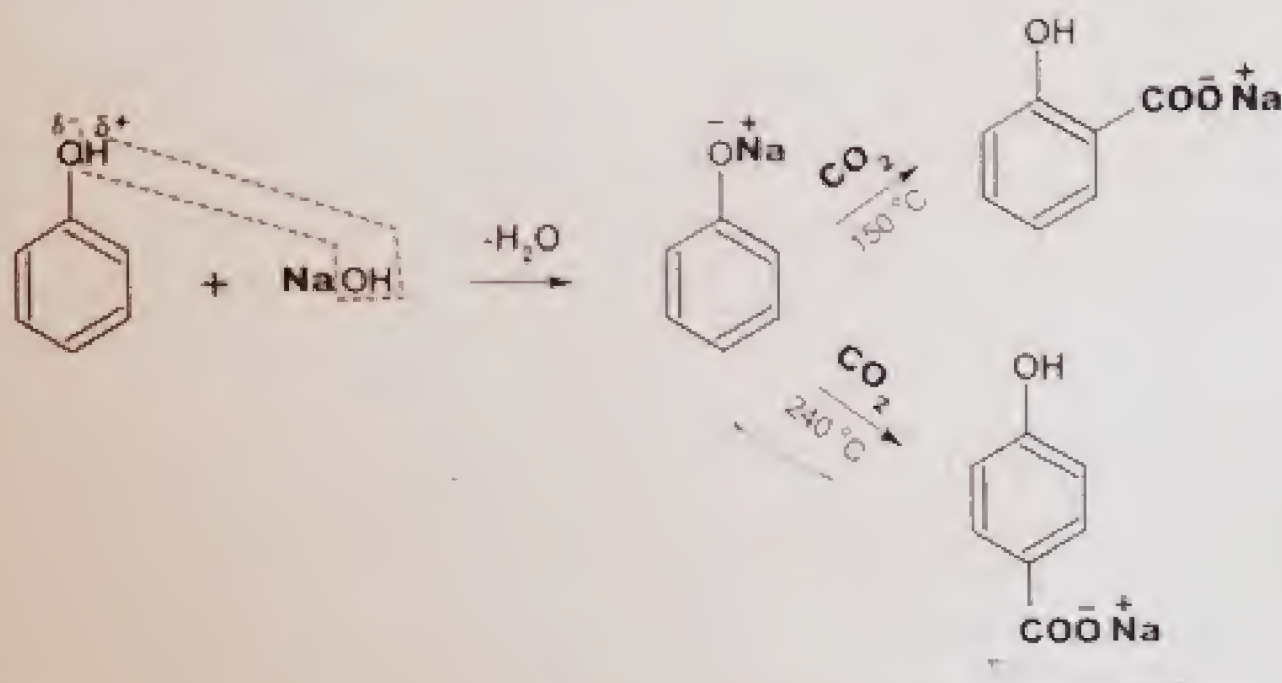


**(1) REACTION WITH SODIUM METAL: CARBOXYLATION OF PHENOLS (KOLBE-SCHMITT REACTION)**

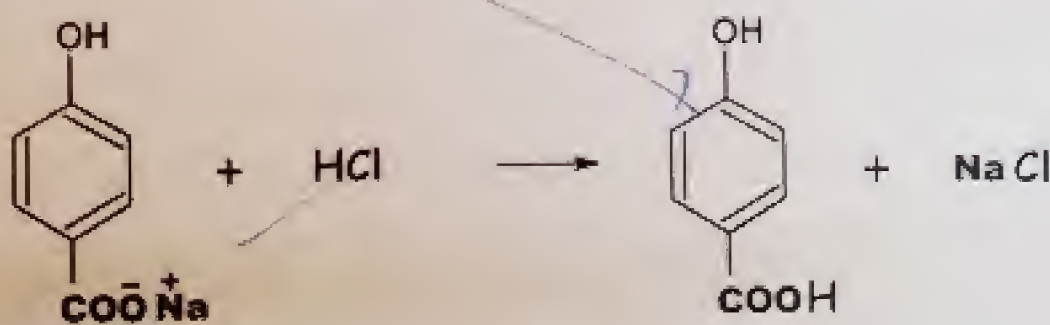
**Quick Quiz-2 (4):** Explain carbonation of phenols.

*CO<sub>2</sub> Addition*

- The reaction of sodium salt of phenol with CO<sub>2</sub> is called Kolbe reaction. It is carbonation of phenol.
- At low temperature, sodium salicylate (sodium-o-hydroxy benzoate), while at higher temperature o-product isomerizes to p-isomer,



- Carbon of CO<sub>2</sub> acts as electrophilic centre in this reaction. Acidification of the salt gives corresponding hydroxyl acid.



*carboxylic acid*

**(2) Oxidation of Phenols**

- Phenols are very reactive towards oxidizing agents.
- The oxidation takes place through several steps which finally destroys the ring




## DIFFERENCE BETWEEN ALCOHOLS AND PHENOL

The main difference between alcohols and phenols are as follow:

### Alcohol:

- The compounds in which hydroxyl group is attached to an alkyl group.
- Alcohols are hydroxyl derivatives of alkanes.
- The compounds in which one hydrogen of water is replaced by an alkyl group.
- The general formula of alcohol is  $R-OH$ .
- Alcohols may be monohydric and polyhydric depending on the number of  $-OH$  groups attached.
- Lower alcohols are generally colorless liquids.
- Alcohols have a characteristic sweet smell and burning taste.
- They are readily soluble in water but solubility decreases in higher alcohols.
- Alcohol reacts with other reagents in two ways, either in which  $C-O$  bond breaks or in which  $O-H$  bond breaks.

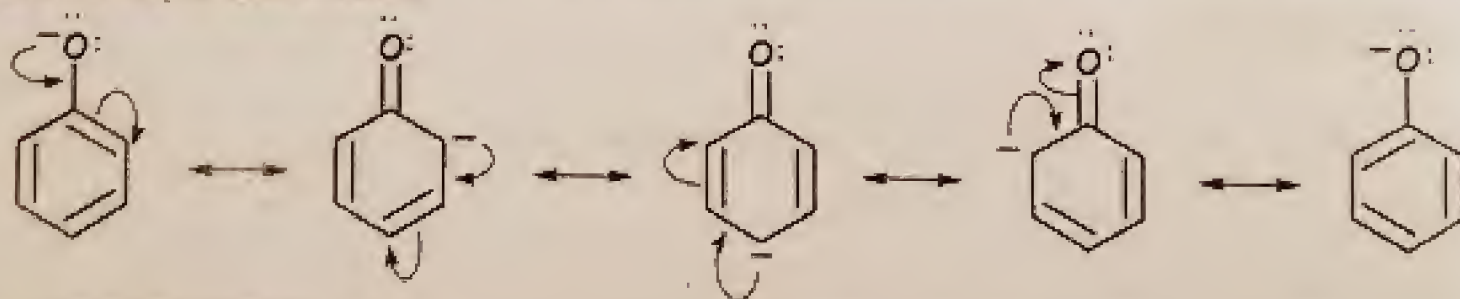
### Phenol:

- The compounds in which hydroxyl group is attached to an aryl group.
- Phenols are derivatives of benzene.
- The compounds in which one hydrogen of water is replaced by an aryl group.
- The general formula of phenol is . It is also known as carbolic acid.
- Phenols are not monohydric or polyhydric.
- They are colorless, crystalline, deliquescent solids.
- They have characteristic phenolic odor.
- Its melting point is  $41^\circ C$ .
- Phenols are more acidic ( $pK_a \approx 10$ ) than alcohols ( $pK_a \approx 16 - 20$ ).
- It is sparingly soluble in water forming pink solution at room temperature but completely soluble above  $68.5^\circ C$ .
- Phenolate ions have resonance structures but alcohols do not have such type structures.

## QUICK QUIZ (2)

(1) How negative charge of phenolate ion is stable?

The negative charge of the phenolate ion is stabilized by resonance due to electron delocalization onto the benzene ring as shown below:



(2) What is acidity order of phenols

Electron withdrawing groups increases the acidity of phenols while electron withdrawing groups decreases the acidity of phenols.

Thus, nitrophenols are stronger than phenol while methyl phenols are weaker than phenols.

So, with these phenols the order is (**more acidic**) nitrophenols > phenol > methyl phenol (**less acidic**)



(3) Why phenols are very reactive towards electrophilic aromatic substitution

- Phenols are very reactive towards electrophilic aromatic substitution.
- The OH group is an ortho- / para- director therefore it produces ortho- / para- products
- The OH group is an electron donating group and it donates electrons to the benzene ring. Thus, it activates the ring. Hence, mild conditions are needed for phenol than that for benzene.

(4) Explain carbonation of phenols.


Page

(5) Alcohols and phenols both contain -OH group. What is difference between them?

In alcohols the OH group is directly attached to an alkyl group. Its general formula is R-OH

e.g.  $\text{CH}_3 - \text{OH}$  (Methanol)

In phenols the OH group is directly attached to an aromatic ring. Its general formula is Ar-OH

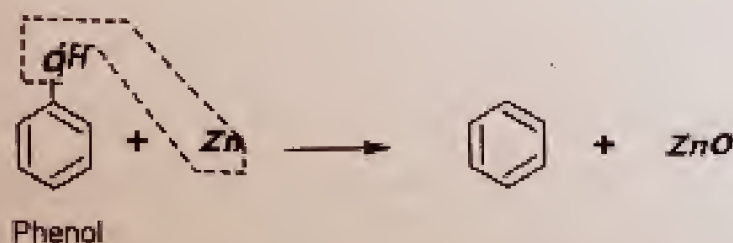
e.g.  -OH (phenol)

(6) Why phenol is more acidic than ethyl alcohol?

The anion of phenol is stabilized by resonance. The anion of ethyl alcohol cannot be stabilized by resonance. Generally, greater the stability of anion, higher the acidity. So, due to greater stabilization of anion of phenol, it is more acidic than ethanol.

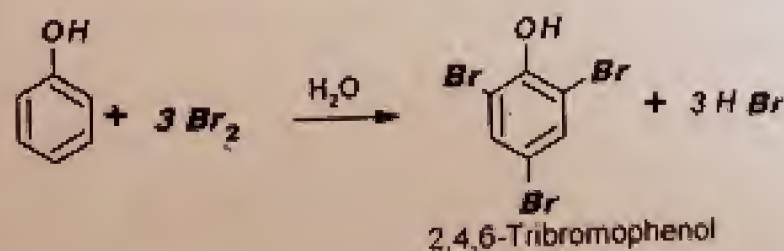
(7) What happens when phenol is heated with zinc dust

Benzene is obtained by distilling phenol with Zinc dust.



(8) What happens when phenol is treated with bromine water?

Aqueous solution of phenol reacts with bromine water to give white precipitates of 2,4,6-tribromophenol. The red colour of bromine water is discharged. This test is used for identification of phenol.





## ETHERS

The compounds in which both hydrogen atoms of water are replaced by alkyl or aryl groups are called ethers.

These have general formula  $R_1 - O - R_2$

Where  $R_1$  and  $R_2$  are alkyl or aryl groups

Ethers are classified into two categories.

If  $R_1 = R_2$ , the ether is called simple or symmetrical ether, e.g.  $CH_3 - O - CH_3$

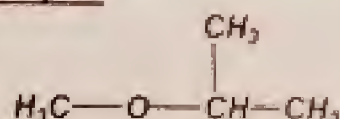
If  $R_1 \neq R_2$ , the ether is called mixed or unsymmetrical ether, e.g.  $CH_3 - O - C_2H_5$

### NOMENCLATURE

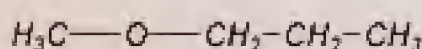
#### (i) Common System of Naming:

In common system of naming simple and mixed (or unsymmetrical) ethers are named by naming the two groups bonded to oxygen followed by the word ether.

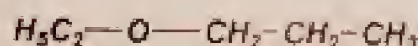
##### Examples



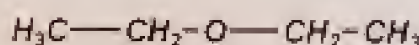
Methyl iso-propyl ether



Methyl n-propyl ether



Ethyl n-propyl ether

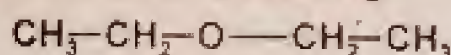


Diethyl ether

**Exercise Q2 (ix)** Write the nomenclature of ether by IUPAC system.

#### (ii) IUPAC System

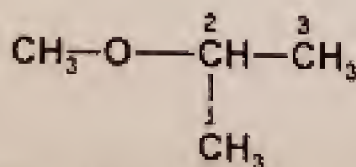
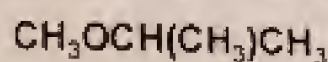
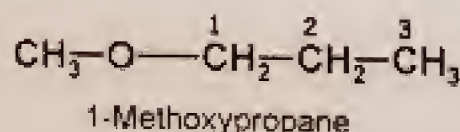
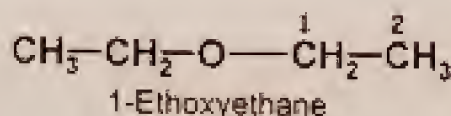
- In IUPAC system of naming simple ethers are named by naming the two groups linked to oxygen atom followed by the word ether, e.g.



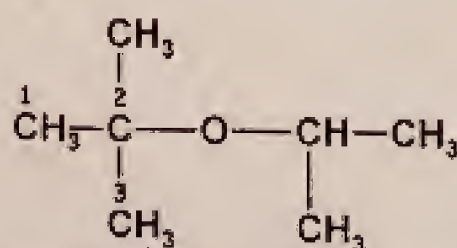
Diethyl ether

- Mixed ethers are named as alkyl derivatives of hydrocarbon. The smaller alkyl group along with oxygen forms the alkoxy substituent.

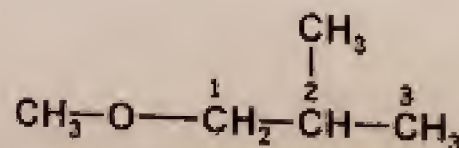
##### Examples



2-Methoxypropane



2-iso-Propoxy-2-methylpropane



1-Methoxy-2-methylpropane



## PREPARATION OF ETHERS

### 1) WILLIAMSON'S SYNTHESIS

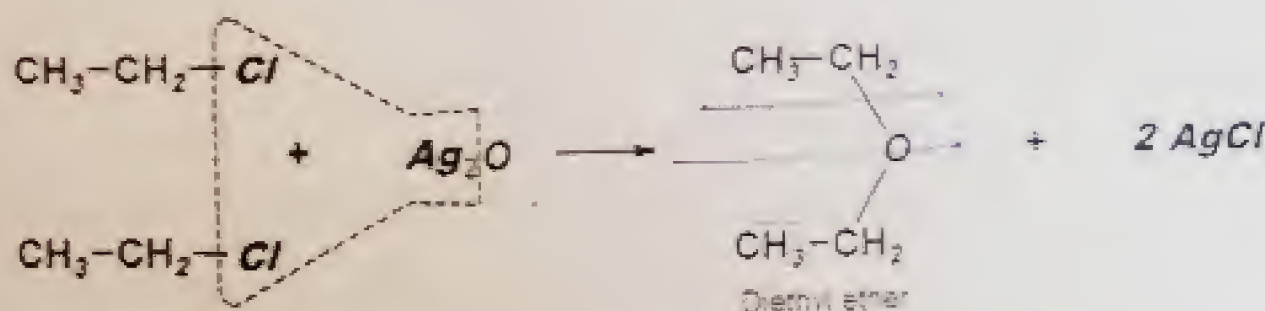


- Alcohols are reacted with metallic sodium to form alkoxides.
- The alkoxide is a strong nucleophile and readily reacts with alkyl halide to produce ether.



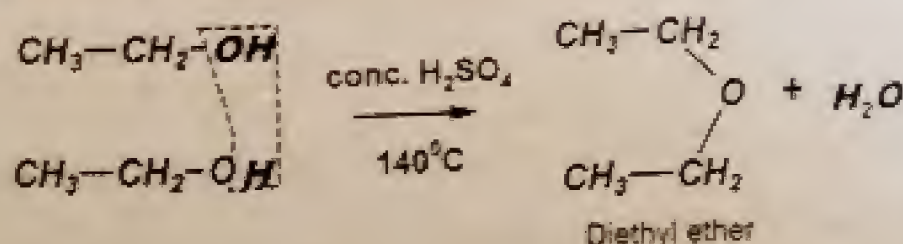
### 2) FROM ALKYL HALIDES AND SILVER OXIDE

Alkyl halides are heated with dry silver oxide to form ethers.



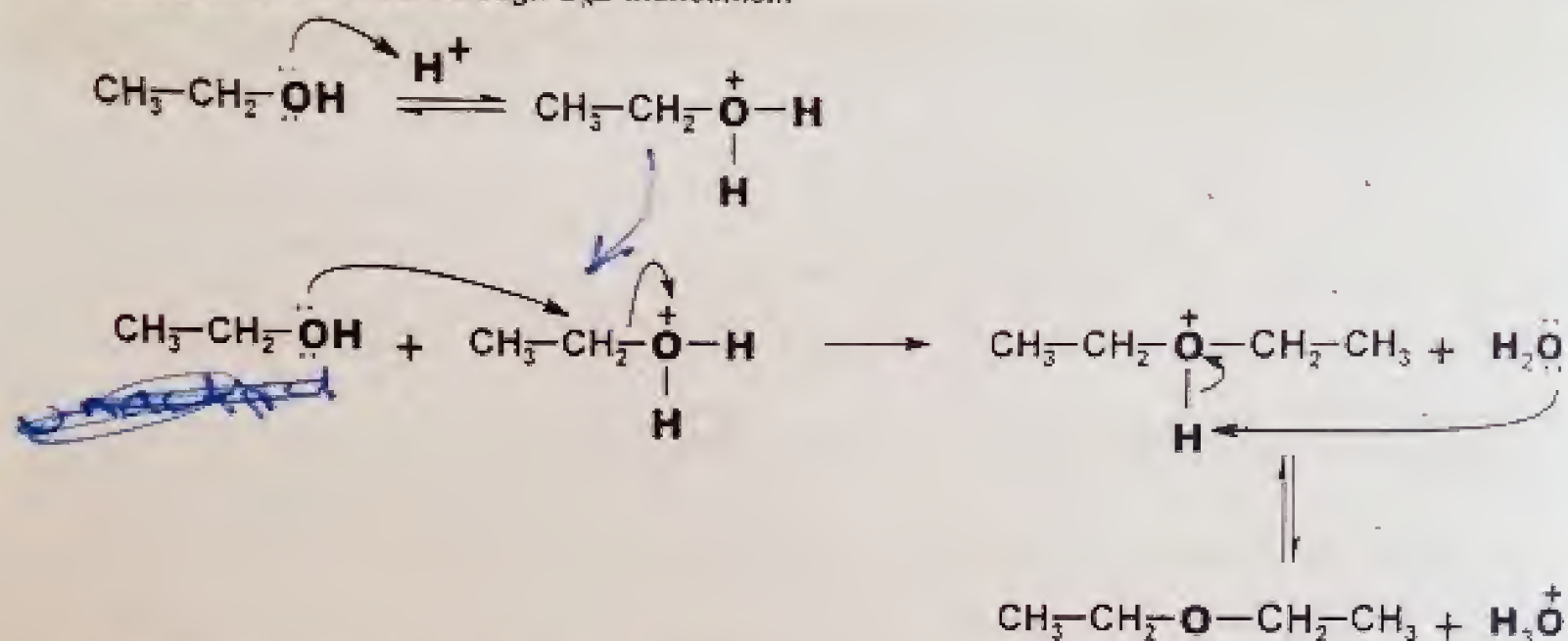
### (III) By Dehydration of Alcohols

By heating excess of alcohol with concentrated  $\text{H}_2\text{SO}_4$  at  $140^\circ\text{C}$ , dehydration to ethers occurs.

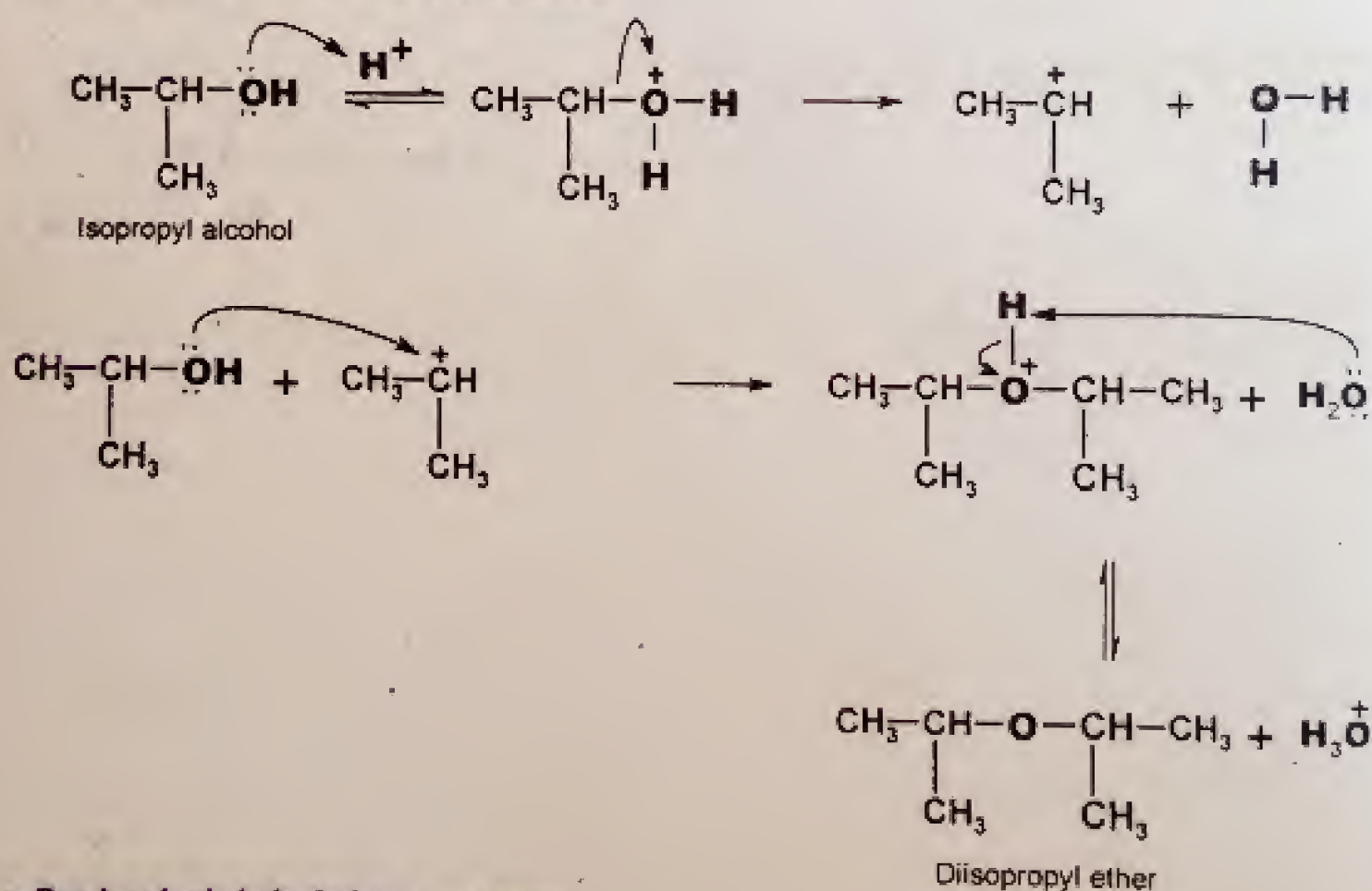




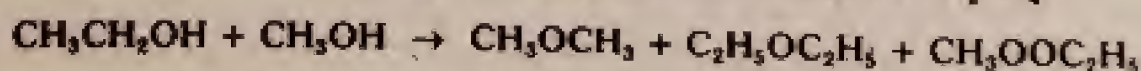
- Primary alcohols react through  $S_N2$  mechanism



- Secondary alcohols react by  $SN_1$ -mechanism



- *ter-Butyl and ethyl alcohol give one ether.*
- Two different primary alcohols give three ethers when treated with  $H_2SO_4$ .



### PHYSICAL PROPERTIES:

- Ethers are colorless, low boiling, highly inflammable compounds.
- Their chemical inactivity and their ability to dissolve fats, oil, gum and many other organic compound make them very good solvent.
- Ethers are soluble in concentrated sulphuric acid, a characteristic of oxygen containing compounds. This property is used as a test to distinguish between ethers and saturate hydrocarbons.



### CHEMICAL REACTIVITY:

The image shows the electrostatic potential for dimethyl ether.

The more **red** an area is, the higher the electron density and the more **blue** an area is, the lower the electron density.

The etheral O atom is a region of high electron density (**red**) due to the lone pairs.

Ether oxygen atoms are Lewis bases.

Like an alcohol -OH group, the -OR group is a poor leaving group and needs to be converted to a better leaving group before substitution can occur.

The most important reaction of ethers is their cleavage by strong acids such as HI or HBr.



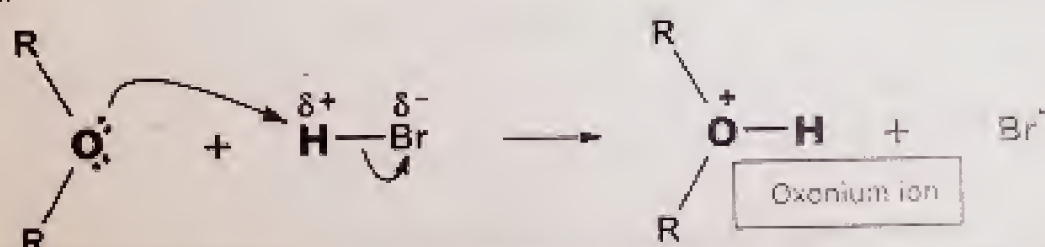
### (1) RESISTANCE TO OXIDATION:

How ethers show resistance to oxidation?

Ethers are resistant to attack by the usual chemical oxidizing agents. Moreover, reagent like  $\text{NH}_3$ , Na, alkali and acids have no action on ethers.

### (2) REACTION WITH H-BR:

The oxygen atom of an ether molecule possesses unshared electron pair, which, accepts a portion of H-Br: to form oxonium ion.

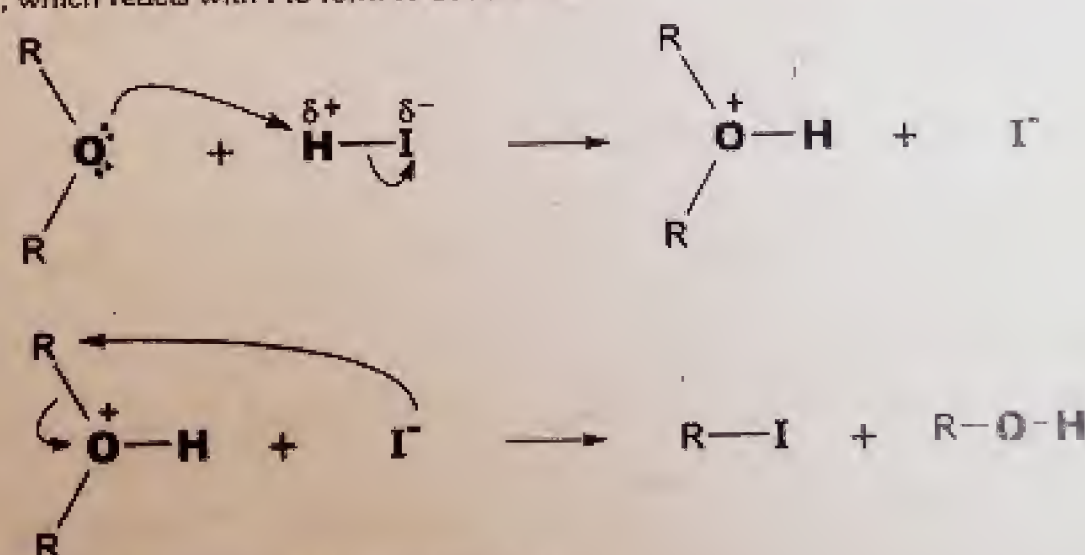


No further reaction takes place.

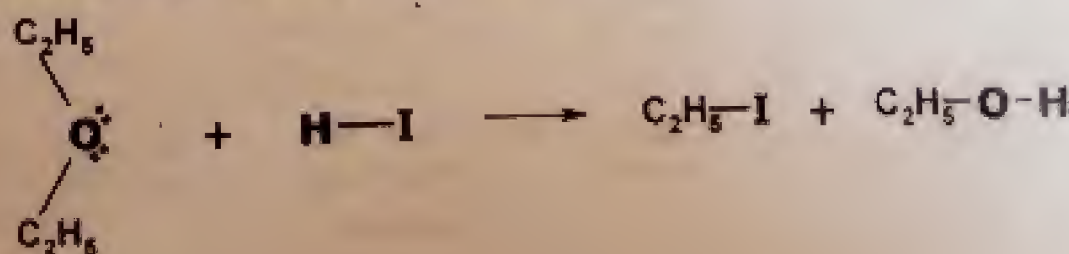
A species with trivalent oxygen and carrying a positive charge on oxygen atom is called an oxonium ion

### (3) REACTION WITH H-I:

The oxygen atom of an ether molecule possesses unshared electron pair, which accepts a proton of H-I to form oxonium ion, which reacts with I to form R-OH and RI.



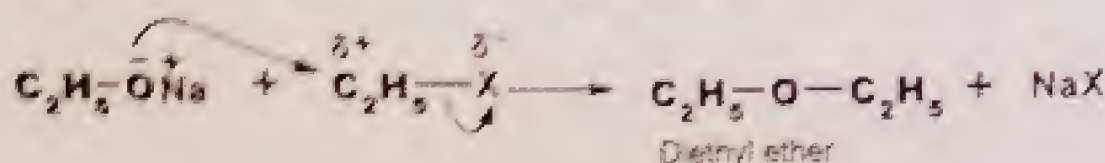
Diethyl ether reacts with HI to form  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{C}_2\text{H}_5\text{I}$ .





## QUICK QUIZ (3)

(1) How is diethyl ether prepared in the laboratory?



(2) What are symmetrical and unsymmetrical ethers?

The compounds in which both hydrogen atoms of water are replaced by alkyl or aryl groups are called ethers.

These have general formula  $\text{R}_1-\text{O}-\text{R}_2$ . Where  $\text{R}_1$  and  $\text{R}_2$  are alkyl or aryl groups

(a) If  $\text{R}_1 = \text{R}_2$ , the ether is called simple or symmetrical ether. e.g.  $\text{CH}_3-\text{O}-\text{CH}_3$

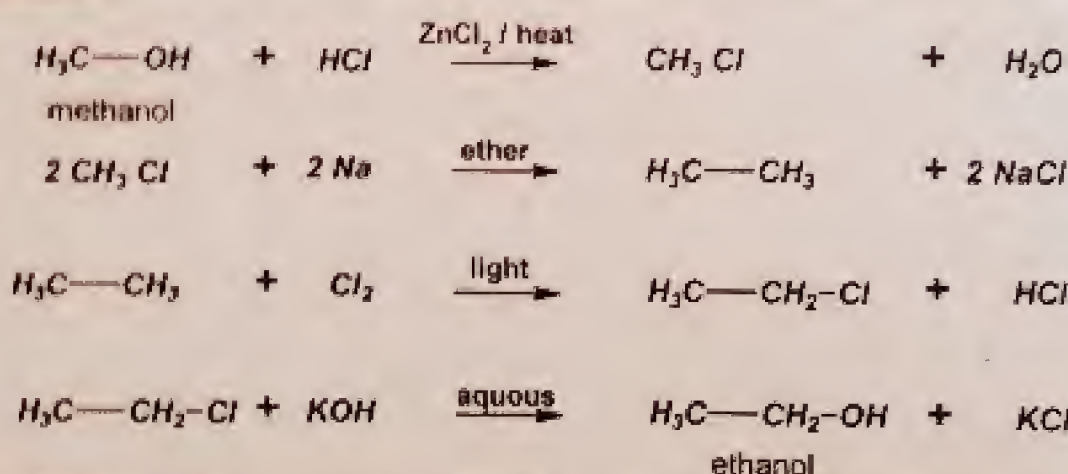
If  $\text{R}_1 \neq \text{R}_2$ , the ether is called mixed or unsymmetrical ether. e.g.  $\text{CH}_3-\text{O}-\text{C}_2\text{H}_5$

(2) What is Williamson's synthesis? It is a method of preparation of ethers.

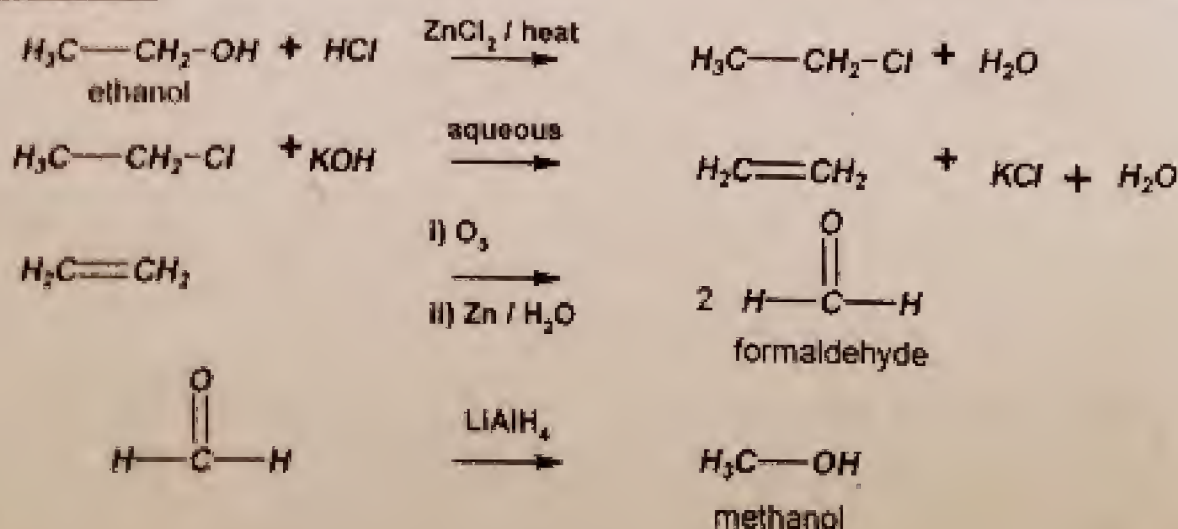


## SOME IMPORTANT CONVERSIONS

(i) Methanol into ethanol

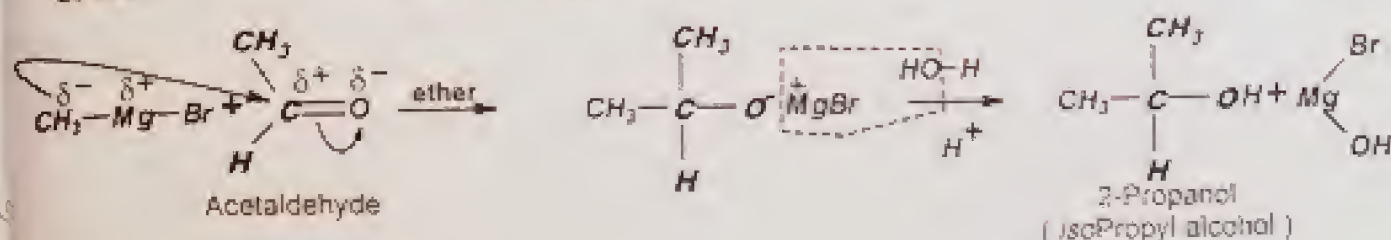
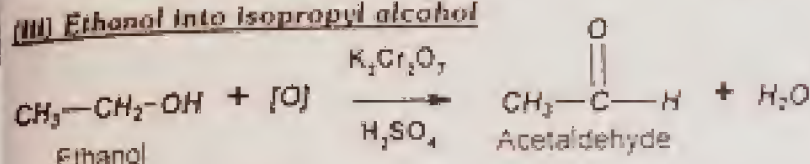


(ii) Ethanol into methanol

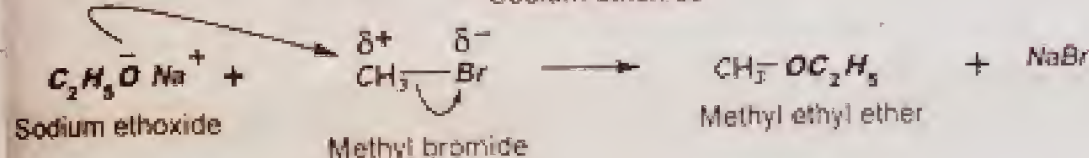




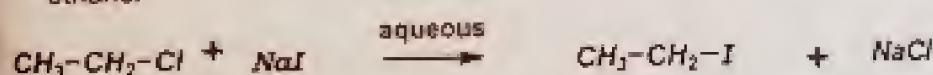
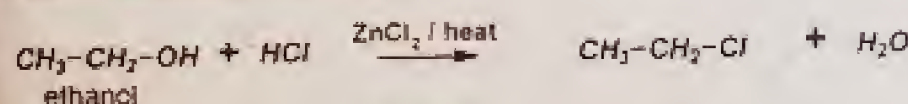
**(iii) Ethanol into isopropyl alcohol**



**(iv) Ethanol into ethyl methyl ether**



**(v) Ethyl alcohol to ethyl iodide**



**SOCIETY, TECHNOLOGY AND SCIENCE**

**1. ANTISEPTICS AND DISINFECTANTS**

- Antiseptics and disinfectants are an essential part of infection control practices and aid in the prevention of nosocomial infections.
- They are extensively used in hospitals and other health care settings for a variety of topical and hard surface application.
- A wide variety of active chemical agents or biocides are found in these products many of which have been used for hundred of years for antiseptics, disinfection and preservation.
- In general, biocides have a broader spectrum of activity than antibiotics.
- The widespread use of antiseptic and disinfectant products has promoted some speculation on the development of microbial resistance, in particular cross-resistance to antibiotics.
- Anti microbial activity of antiseptics and disinfectants can be influenced by many factors e.g. formulation effects, presence of an organic load, temperature, dilution etc.

**Antiseptics**

**An antiseptic is a substance which inhibits the growth and development of micro organisms.**

- A antiseptics are thought of as topical agents for application to skin, mucous membrane and inanimate objects. They can be either bactericidal or bacteriostatic.
- Their uses include cleansing of skin, and wound, surfaces after injury preparation of skin surface prior to injection or surgical procedure and routine disinfection or surgical procedure and routine disinfection of oral cavity as par of oral hygiene.



### Disinfectants

- Disinfectants were introduced by Lister who introduced carbolic acid (phenol) as the first disinfectant.
- Today disinfectants are widely used in the health care, food and pharmaceutical sectors to prevent unwanted micro-organisms from causing disease.
- Disinfectants chemicals disrupt significant cellular structures or processes in order to kill or eliminate micro-organisms.

### 2. ETHER - AN EFFECTIVE ANAESTHETIC

- Before the advent of anaesthetics, surgery was a savage and primitive affair. It was agony for the patient, and surgeons were therefore only prepared to operate if it was absolutely essential, for example the amputation of a damaged limb that would otherwise become gangrenous. Anaesthetics enable surgery to develop from crude carpentry to its present sophisticated forms.
- Three of the most important early anaesthetics were nitrous oxide (dinitrogen oxide,  $N_2O$ ), ether (ethoxyethane,  $CH_3CH_2OCH_2CH_3$ ) and chloroform (trichloromethane,  $CHCl_3$ ). Nitrous oxide is non-toxic and non-flammable, but it only produces light anaesthesia. Chloroform produces deep anaesthesia and is non-flammable, but it is toxic and carries the risk of liver damage.

### KEY POINTS

- Alcohols and phenols are hydroxyl derivatives of aliphatic and aromatic hydrocarbons.
- General formula for alcohol is  $ROH$ , for Phenol  $PhOH$ , and for ether it is  $ROR$ .
- Alcohols are usually named by replacing 'e' from the Alkane with 'ol'.
- Primary alcohols can be oxidized.
- Secondary alcohols can be oxidized to ketones but no further.
- Tertiary alcohols cannot be oxidized (no carbinol  $C-H$ ).
- The thiol functional group consists of an  $S$  atom bonded to a  $C$  atom and a  $H$  atom via  $\sigma$  bonds.
- Thiols are much more acidic than similar alcohols, e.g.  $RSH$  ( $pK_a = 10$ ) versus  $ROH$  ( $pK_a = 16$  to  $19$ ).
- Phenols are more acidic ( $pK_a \approx 10$ ) than alcohols ( $pK_a \approx 16 - 20$ ), but less acidic than carboxylic acids ( $pK_a \approx 5$ ).
- Epoxides are more reactive than simple ethers.
- In IUPAC system, ethers are named as alkoxy derivatives of alkanes.
- In contrast to alcohol, ethers are fairly unreactive.
- Alcohols are soluble in water while phenols are sparingly soluble.
- General formula for alcohol is  $R-OH$  while for phenol is  $Ar-OH$ .
- Methyl alcohol has proved to be excellent fuel for racing car.
- Ethyl alcohol may be the first organic chemical routinely manufactured by humans.
- Ethyl alcohol is also named as wine, beer and whiskey.
- Fuel oil mainly consists of amyl alcohol ( $C_5H_{11}OH$ ).
- 95% ethyl alcohol is known as rectified spirit or commercial alcohol.
- Ethylene glycol is the major component in commercial coolants and anti-freeze.
- Glycerol is an excellent moisture retaining agent. It is used in vanishing creams, body lotions shaving foams and tooth pastes.
- Bakelite (plastic) is phenol form aldehyde resin.
- Phenol is used as starting material for drugs such as salol, aspirin, phenolphthalein and several other dyes.
- Diethyl ether has been used in surgery for anaesthesia.
- Cyclic ethers are known as epoxides.



## EXERCISE

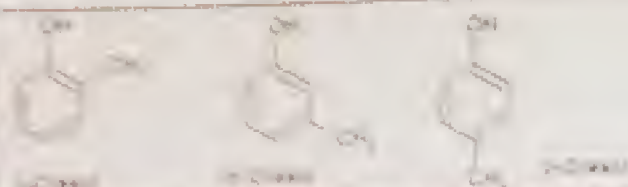
**Q1: Select the right answer from the choices given with each question.**

- Which compound shows hydrogen bonding?  
(a)  $C_2H_6$  (b)  $C_2H_5Cl$  (c)  $CH_3-O-CH_3$  (d)  $C_2H_5OH$
- Which compound is called a universal solvent?  
(a)  $H_2O$  (b)  $CH_3OH$  (c)  $C_2H_5OH$  (d)  $CH_3-O-CH_3$
- According to Lewis concept ethers behave as  
(a) Acid (b) Base (c) Acid as well as base (d) None of them
- Ethanol can be converted into ethanoic acid by  
(a) Hydrogenation (b) Hydration (c) Oxidation (d) Fermentation
- Ethanol is denatured by adding;  
(a) methanol (b) Carboic acid (c) Acetone (d) Propanol
- When phenol reacts with  $CH_3COCl$  the product formed is;  
(a) Ether (b) Alcohol (c) Aldehyde (d) Ester
- Williamson's synthesis of ethers is superior to alcohols because it makes  
(a) Symmetrical ethers (b) Asymmetrical ethers  
(c) Ether at room temperature (d) Both symmetrical and asymmetrical Ethers.
- A methyl phenol is also called  
(a) A cresol (b) Benzyl alcohol (c) Alcohol (d) Formaldehyde
- Which one of the following compounds does not contain carboxylic group?  
(a) Acetic acid (b) Formic acid (c) Benzoic acid (d) Picric acid
- Hydrogen bonding is maximum in  
(a) Diethyl ether (b) Ethanol (c) Ethyl alcohol (d) Triethyl amine
- Which of the following compounds have no attraction at all with water?  
(a)  $C_6H_6$  (b)  $C_2H_5OH$  (c)  $CH_3CH_2CH_2OH$  (d)  $CH_3-O-CH_3$
- Phenols are more acidic than alcohols which statement is correct?  
(a) Phenol turns blue litmus paper red (b) Alcohol liberates  $CO_2$  with carbonate solution  
(c) Phenoxide ion is stabilized due to resonance (d) Alkoxide ion is stabilized due to resonance
- Carboic acid is treated with dilute nitric acid at  $25^\circ C$ , the product is  
(a) o-nitrophenol (b) p-nitrophenol (c) m-nitrophenol (d) Both a and b
- Oxonium ion is formed when  
(a) Ethanol reacts with Na metal (b) Phenol reacts NaOH solution  
(c) Ether is treated with HI (d) Ethanol is treated with aq. NaOH and iodine
- 2,4,6-Tribitrophenol is commercially called as  
(a) TNT (b) Picric acid (c) Carboic acid (d) Fumaric acid

## ANSWERS TO MULTIPLE CHOICE QUESTIONS

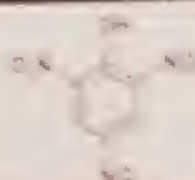
(i) Ans: (d) $C_2H_5OH$ $C_2H_5OH$ shows hydrogen bonding, since it contains OH group.	(ii) Ans: (a) $H_2O$ $H_2O$ is called as universal solvent since it can dissolve a large number of chemical substances
(iii) Ans: (b) Base According to Lewis concept, a base is defined as "Electron Pair Donor" specie. Since ether has lone pairs of electrons on oxygen atom, $(R-\ddot{O}-R)$ , so it can donate these and thus it can behave as a Lewis base.	(iv) Ans: (c) Oxidation Ethanol is oxidized to ethanol (acetaldehyde) and finally to ethanoic acid (acetic acid) with oxidizing agents such as $K_2Cr_2O_7 + H_2SO_4$
(v) Ans: (a) methanol Methanol is added to ethanol to make it unfit for drinking.	(vi) Ans: (d) Ester $Ph-OH + CH_3COCl \rightarrow CH_3COOPh + HCl$ Phenyl acetate (ester)
(vii) Ans: (d) Both symmetrical and asymmetrical ethers Williamson's synthesis uses an alkoxide and an alkyl halide. Thus, both symmetrical and unsymmetrical ethers can be prepared.	(viii) Ans: (a) A cresol





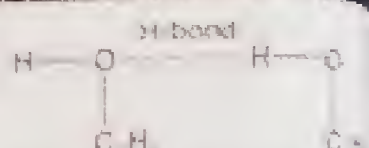
(ix) Ans: (d) Picric acid

Picric acid is 2,4,6-Trinitrophenol



(x) Ans: (b) Ethanol or (c) Ethyl alcohol

Both alcohol or ethanol.  
Both molecule hydrogen bonding due to OH group.



(xi) Ans: (a)  $C_6H_6$

It is benzene. It is a highly symmetric hydrocarbon. So, it will have no attraction for polar water molecules.

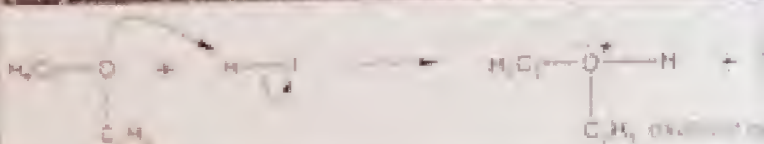
(xii) Ans: (c) Phenoxide ion is stabilized due to resonance

Phenoxide shows such behaviour due to the formation of resonance structures (phenoxide ion).

(xiii) Ans: (d) Both a and b

Catechol and is phenol. It has OH group on adjacent carbons. The OH group is an ortho-director in electrophilic and p-nitrophenol are produced.

(xiv) Ans: (c) Ether is treated with HI



(xv) Ans: (b) Picric acid

See MCQ no. (x).

## Q2: Give brief answers for the following questions.

(i) What are alcohols? How are they classified?

The aliphatic organic compounds containing hydroxyl group  $-OH$ , as functional group are called alcohols.

**Monohydric alcohols:** Alcohols containing one  $-OH$  group are called monohydric alcohols.

**Polyhydric alcohols:** The alcohols containing two or more hydroxyl groups are known as polyhydric alcohol.

**Classification of Monohydric Alcohols:**

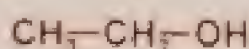
Monohydric alcohols are classified into the following three families.

(i) Primary alcohols

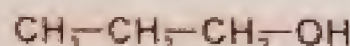
In these, carbon atom attached to OH group, is directly attached to one or no carbon atom.



Methanol



Ethanol



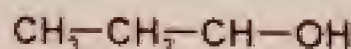
1-Propanol  
(n-propyl alcohol)

(ii) Secondary alcohols

In these, carbon atom attached to OH group, is directly attached to two carbon atoms.



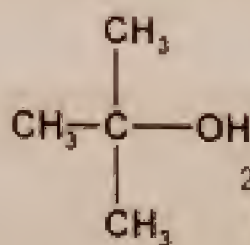
$\begin{array}{c} | \\ CH_3 \end{array}$  2-Propanol  
(sec-Propyl alcohol)



$\begin{array}{c} | \\ CH_3 \end{array}$  2-Butanol  
(sec-Butyl alcohol)

(iii) Tertiary alcohols

In these, carbon atom attached to OH group, is directly attached to three carbon atoms.



2-Methyl-2-propanol  
(ter-Butyl alcohol)

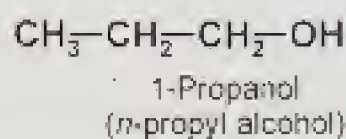
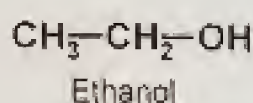
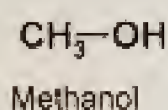


**(III) How are monohydric alcohols classified?**

Monohydric alcohols are classified into the following three families:

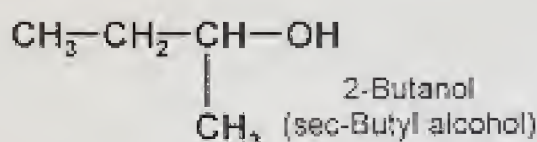
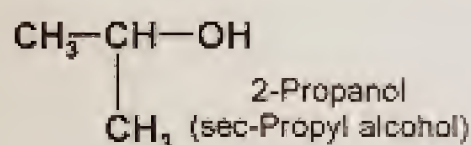
**(i) Primary alcohols:**

In these, carbon atom attached to OH group, is directly attached to one or no carbon atom.



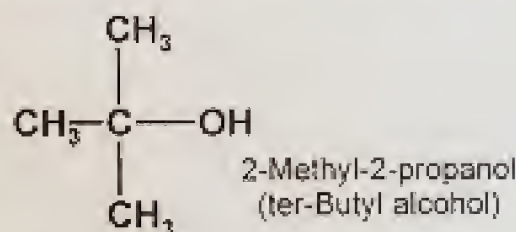
**(ii) Secondary alcohols:**

In these, carbon atom attached to OH group, is directly attached to two carbon atoms.



**(iii) Tertiary alcohols:**

In these, carbon atom attached to OH group, is directly attached to three carbon atoms.



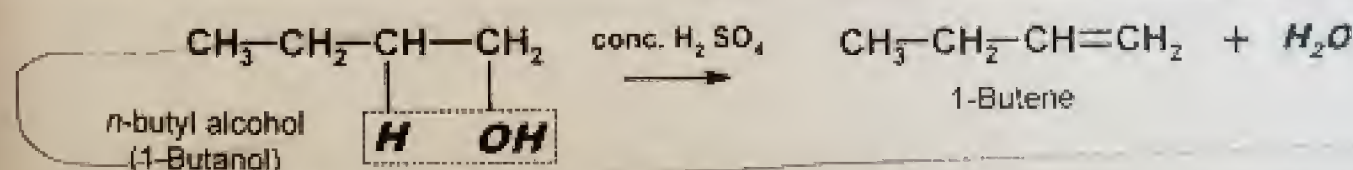
**(III) Compare the acidity of primary, secondary and tertiary alcohols.**

- Due to the electronegativity of the O atoms, alcohols are slightly acidic.
- The anion derived by the deprotonation of an alcohol is the **alkoxide**.

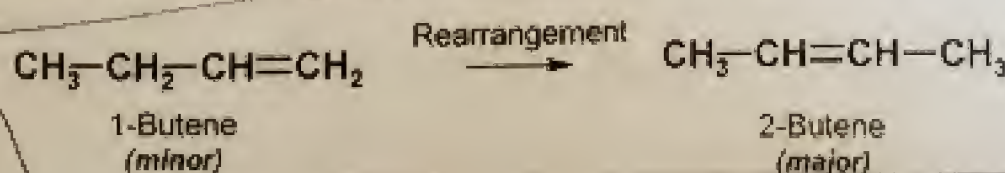


- The alkyl groups attached to  $\alpha$ -carbon atom decreases the acidity.
- Thus primary alcohol is more acidic than secondary which is more acidic than tertiary alcohols.

**(iv) 2-Butene is the major product when n-butyl alcohol is heated with conc.  $\text{H}_2\text{SO}_4$ . Explain.**



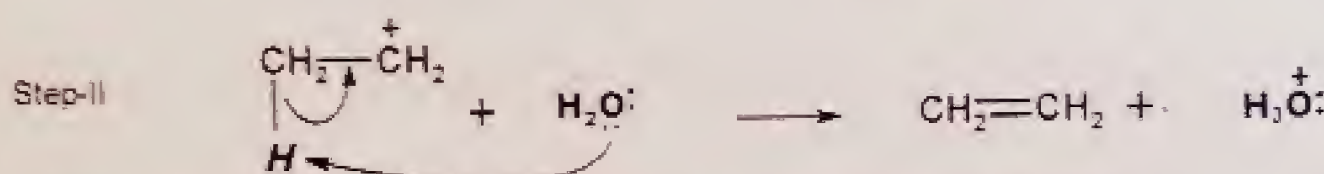
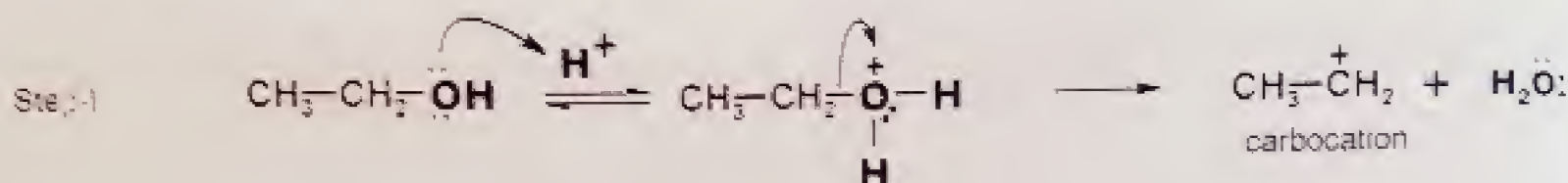
The stability of alkene increases with increase in degree of substitution on double bond. Thus, highly alkylated alkenes are more stable. Since, 1-butene is less alkylated than 2-butene, therefore, under acidic conditions, 1-butene rearranges to 2-butene. Hence, 2-butene is the major product.





(e) Give the mechanism of dehydration of alcohols.

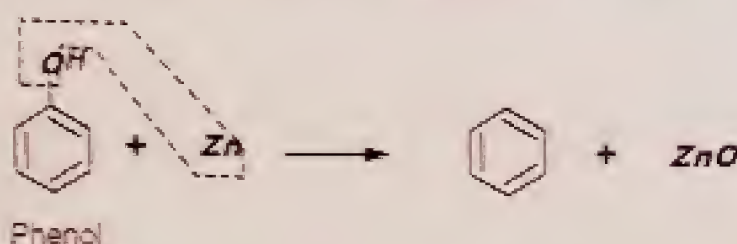
Under acidic conditions, the alcohols dehydrate by E1 mechanism.



**NOTE:** The mechanism for the formation of ethers is given on page 285

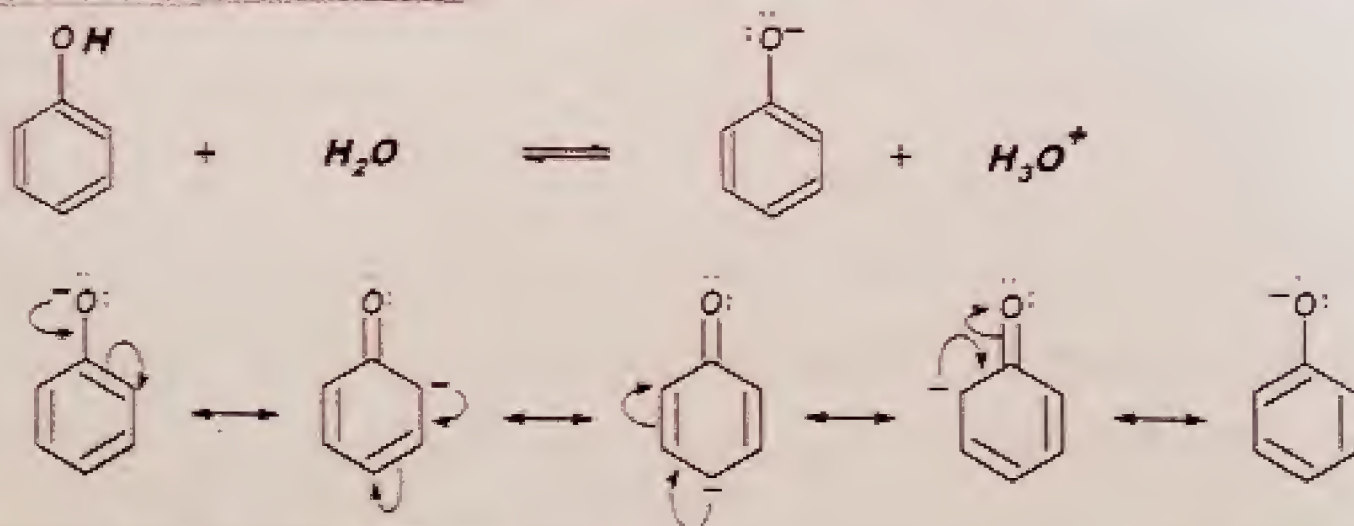
(vi) How will you obtain benzene from alcohol (phenol)?

Benzene is obtained by distilling phenol with Zinc dust.



(vii) Alcohols phenols both have OH group but phenols are more acidic than alcohols.

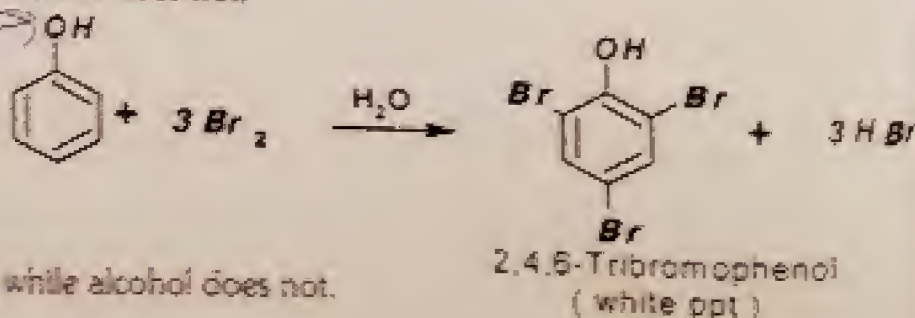
Phenols are more acidic ( $\text{pK}_a = 10$ ) than alcohols ( $\text{pK}_a = 16 - 20$ ). It is because the negative charge of the phenolate ion is stabilized by resonance due to electron delocalization onto the ring. In alcohol there is no resonance stabilization of alkoxide ion.



(viii) How will you differentiate between an alcohol and phenol?

These can be distinguished by following ways

- Phenol gives white ppt with  $\text{Br}_2$  water, while alcohol does not.



- Alcohol is neutral while phenol is acidic.
- Phenol gives deep purple colour with  $\text{FeCl}_3$ , while alcohol does not.



(ix) Write the nomenclature of ether by IUPAC system

See Page 288

(x) Why is phenol more soluble in water than toluene?

Phenol shows polar nature due to presence of OH group. Water is also a polar substance. So, phenol dissolves in water by forming hydrogen bond.

Toluene is a non-polar hydrocarbon. It is unable to develop attractions with polar water molecules. Thus, it is very much less soluble in water than phenol.

### Q3: Give detailed answers for the following questions.

1. How will you prepare alcohols on industrial scale?

#### INDUSTRIAL PREPARATION OF METHANOL

Methyl alcohol is obtained by passing water gas over heated zinc and chromium oxide at 450-500 °C under 200 atmospheric pressure

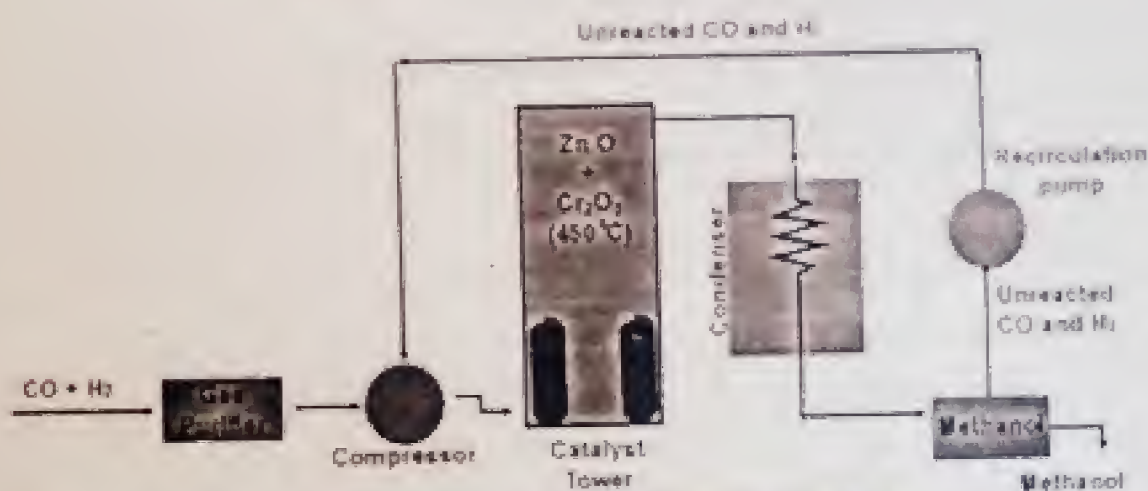
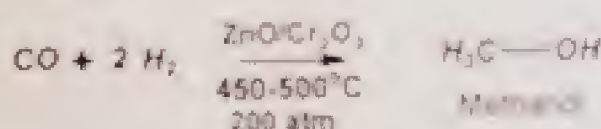


Fig. Flow sheet diagram for the manufacturing of methanol.

- In this process, a mixture of CO and H<sub>2</sub> is purified and compressed under a pressure of 200 atm
- These are then taken to the reaction chamber by coiled pipes where catalyst is heated upto 450 – 500 °C.
- CO and H<sub>2</sub> reacts together to give methanol vapours.
- These vapours are passed through a condenser to get liquid methanol.
- Unreacted gases are recycled through compressor to reaction chamber

#### INDUSTRIAL PREPARATION OF ETHANOL

All over the world ethanol is prepared on industrial scale by the process of fermentation.

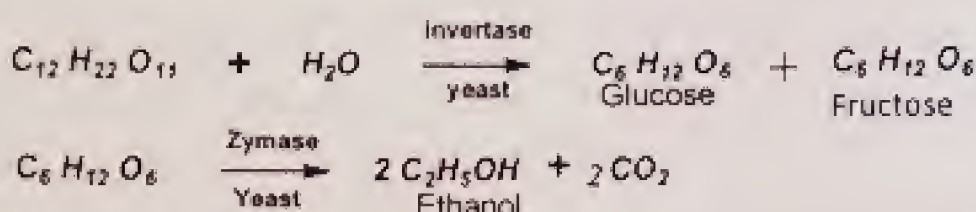
- Fermentation is a bio-chemical process, which occurs in the presence of certain enzymes secreted by micro-organisms such as yeast.
- Optimum temperature for this process is 25-35°C.
- Proper aeration, dilution of solution and absence of any preservative are essential conditions for fermentation.
- In Pakistan ethanol is prepared by the fermentation of molasses, starch grains or fruit juices.



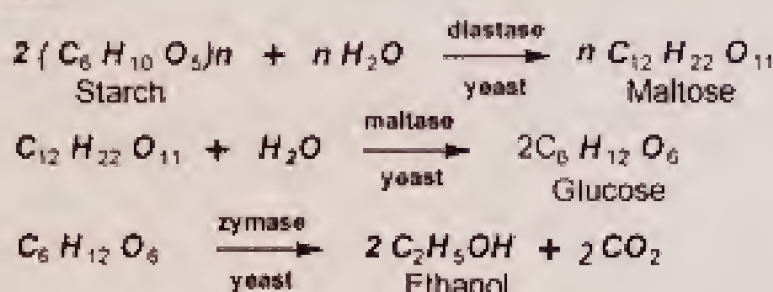
### From Molasses

The residue obtained after the crystallization of sugar from concentrated sugar cane juice is called molasses.

It is fermented by enzymes present in yeast to give ethanol.



### From starch



### Collection of Ethanol

- An alcohol obtained by fermentation is only upto 12%.
- It never exceeds 14% because above this enzymes become inactive.
- This alcohol is distilled again and again to obtain 95% alcohol which is called rectified spirit.
- Absolute alcohol is obtained by re-distillation of rectified spirit in the presence of CaO, which absorbs moisture.

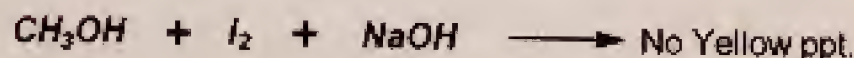
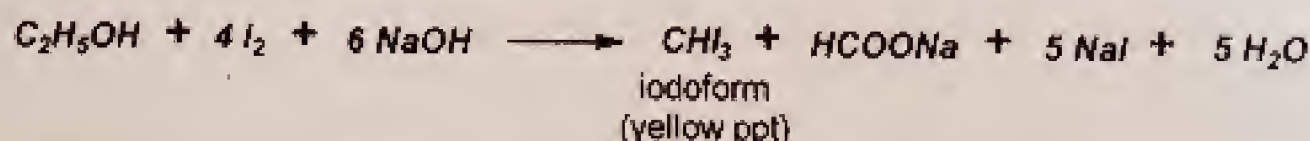
## 2. Distinguish ethanol from methanol and ethanol from phenol.

### Methanol and Ethanol

These can be distinguished by iodoform test

Ethanol gives yellow ppt. of iodoform on reacting with NaOH and I<sub>2</sub>

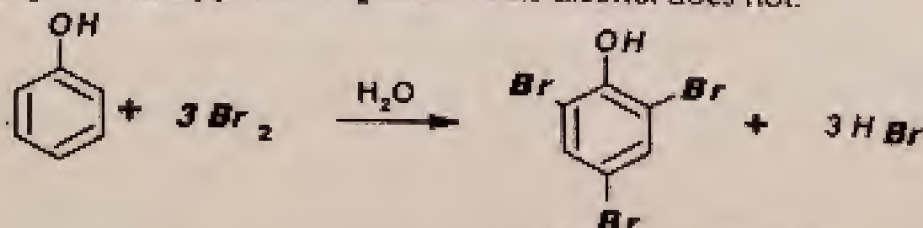
Methanol does not give yellow ppt of iodoform with NaOH and I<sub>2</sub>



### Phenol and Ethanol

These can be distinguished by following ways

- Phenol gives white ppt with Br<sub>2</sub> water while alcohol does not.



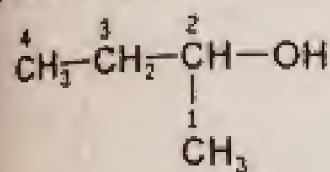
- Alcohol is neutral while phenol is acidic.
- Phenol gives deep purple colour with FeCl<sub>3</sub> while alcohol does not.



3. How will you distinguish between primary, secondary and tertiary alcohols? Explain with reactions.  
See Page 274

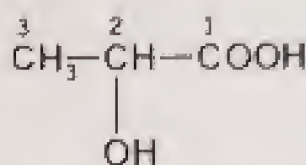
4. Give IUPAC names and structures of the following compounds.

(i) *sec-Butyl alcohol*



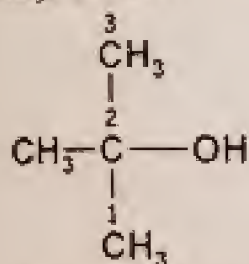
2-Butanol

(ii) *Lactic acid*



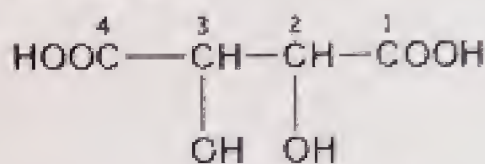
2-Hydroxypropanoic acid

(iii) *ter-Butyl alcohol*



2-Methyl-2-propanol

(iv) *Tartaric acid*



2,3-Dihydroxybutanedioic acid

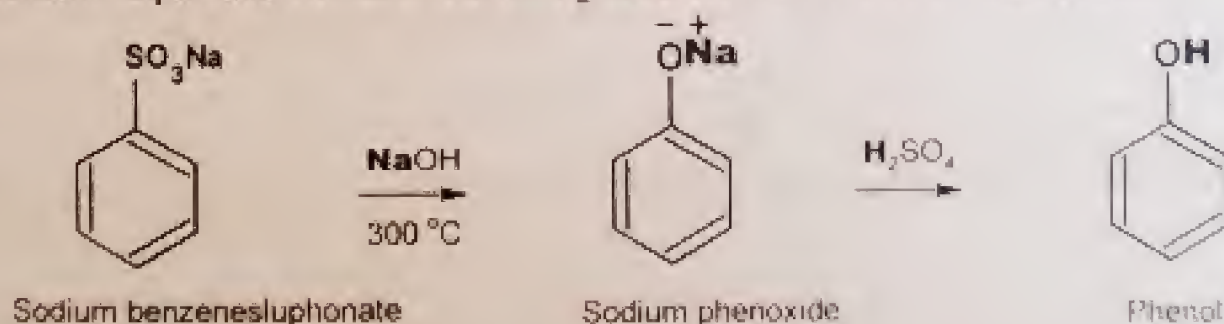
5. Give the reactivity of ethers.

- The ethereal O atom is a region of high electron density due to the lone pairs.
- Ether oxygen atoms are Lewis bases.
- Like an alcohol -OH group, the -OR group is a poor leaving group and needs to be converted to a better leaving group before substitution can occur.
- The most important reaction of ethers is their cleavage by strong acids such as HI or HBr.

6. Give at least two methods for the preparation of phenol.

(1) **Reaction of Benzene Sulfonic Acid with Hydroxide**

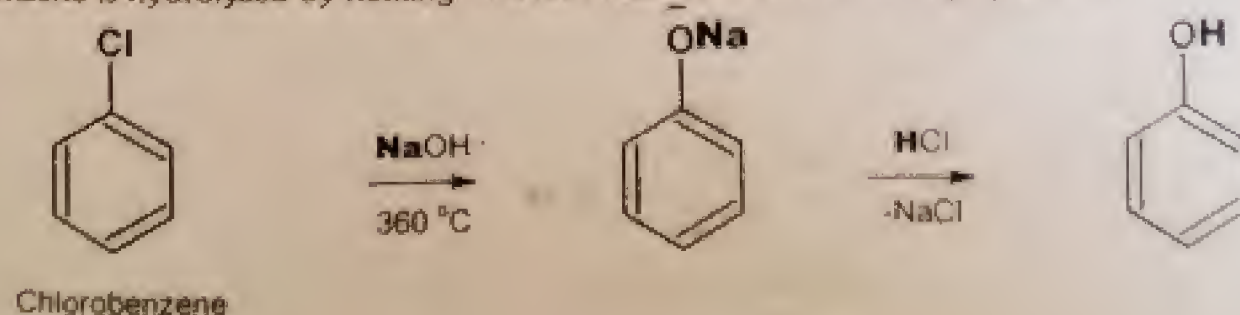
Sodium benzene sulphonate on fusion with strong alkali like NaOH or KOH, yield phenol.



- At such a high temperature, side reactions also occur.

(2) **Base Hydrolysis of Chlorobenzene**

Chlorobenzene is hydrolyzed by heating with NaOH at 360°C and under high pressure.

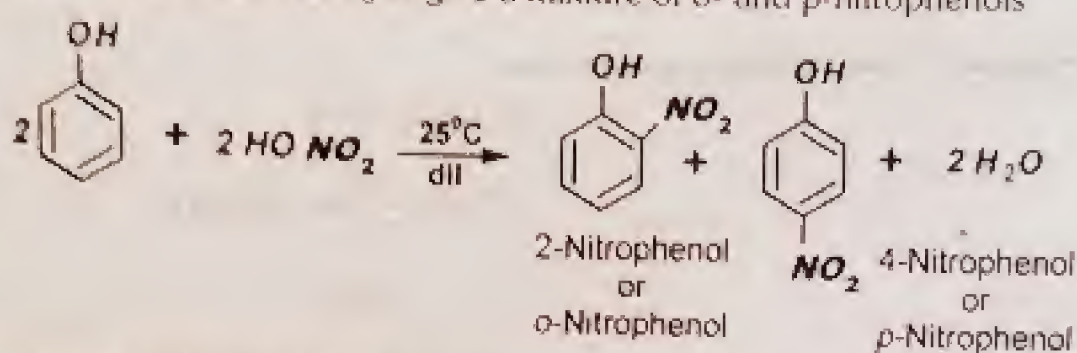




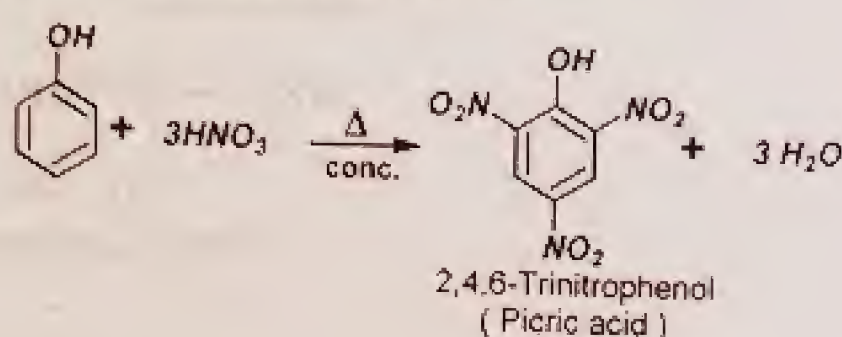
7. How does phenol react with;

(i)  $\text{HNO}_3$

Phenol reacts with dil.  $\text{HNO}_3$  to give a mixture of o- and p-nitrophenols

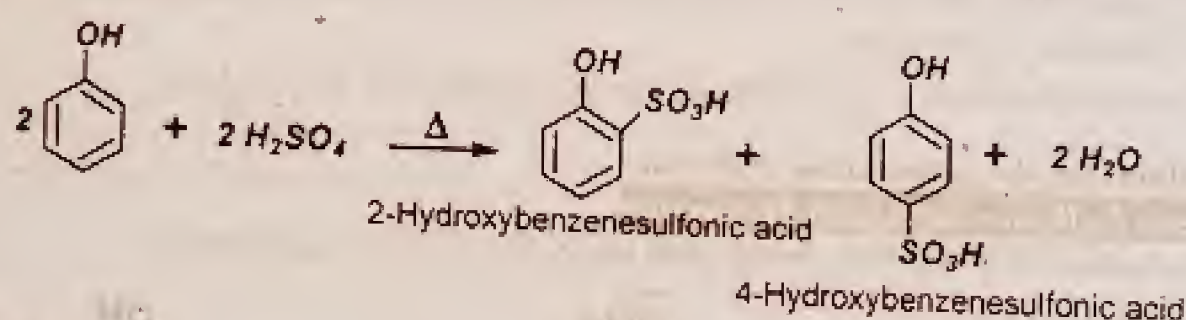


Phenol reacts with conc.  $\text{HNO}_3$  to give picric acid



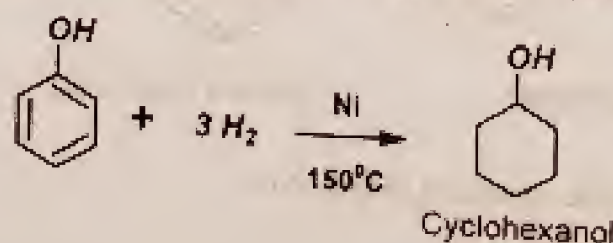
(ii)  $\text{H}_2\text{SO}_4$

- Phenol reacts with conc.  $\text{H}_2\text{SO}_4$  at room temperature to give o- and p-hydroxybenzenesulphonic acids.
- At  $20^\circ\text{C}$  o-isomer is formed in greater percentage, while at  $100^\circ\text{C}$ , p-isomer is formed in greater percentage.



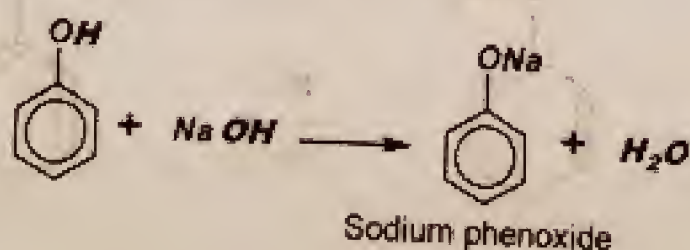
(iii)  $\text{H}_2/\text{Pt}$

When hydrogen is passed through phenol at  $150^\circ\text{C}$  in the presence of Ni catalyst it gives cyclohexanol.



(iv)  $\text{NaOH}$

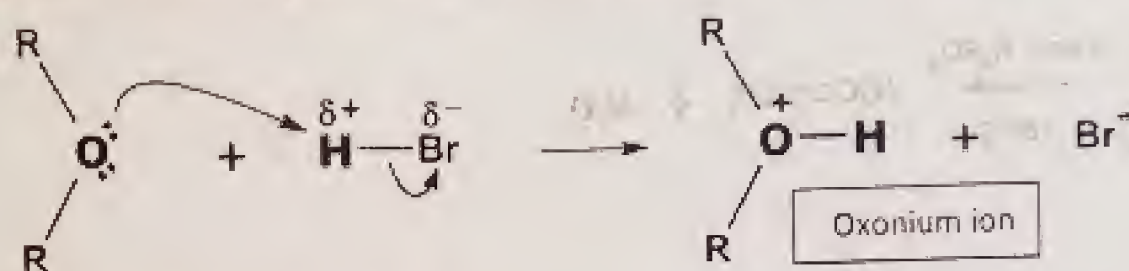
Phenol reacts with alkalis to form salts, e.g.





8. What is oxonium ion? Describe the chemical reactivity of ether.

A species with trivalent oxygen and carrying a positive charge on oxygen atom is called an **oxonium ion**.

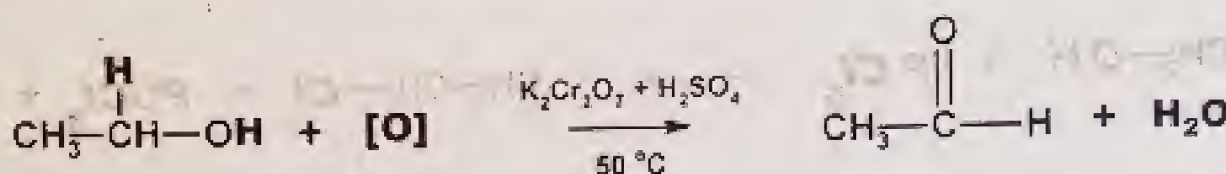


(For reactivity of ether see Q5)

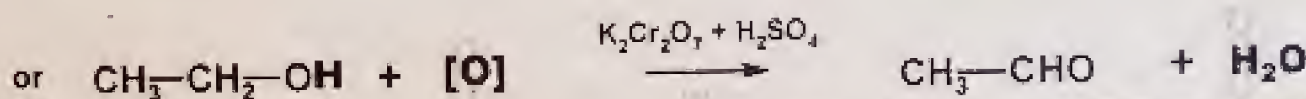
9. Explain following terms using ethyl alcohol as an example;

(i) **Oxidation**

A primary alcohol is first oxidized to an aldehyde, which is further oxidized to a carboxylic acid.



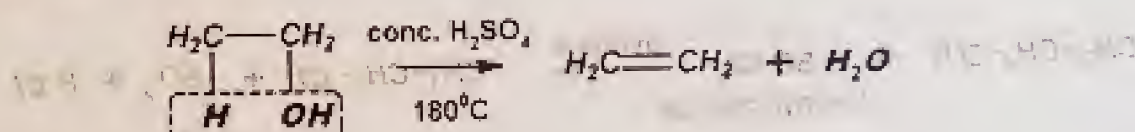
Ethanol



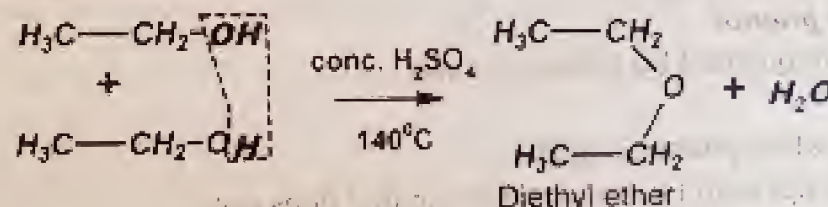
(ii) **Dehydration**

Alcohols react with conc.  $\text{H}_2\text{SO}_4$  and give different products at different temperatures.

High temperature, low alcohol conc.

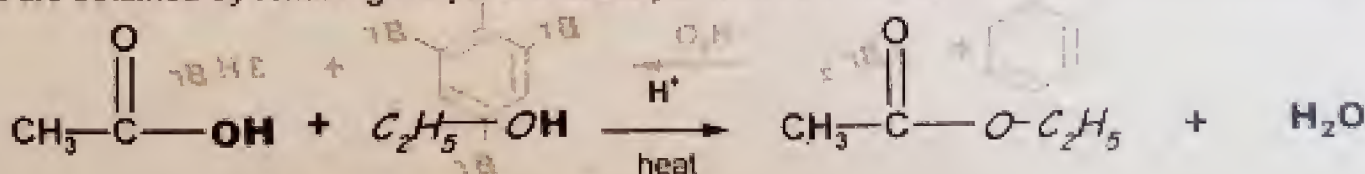


Low temperature, high alcohol conc.

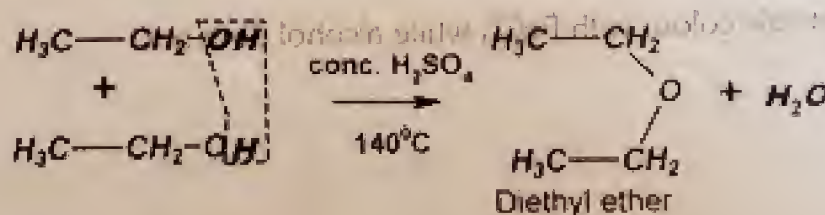


(iii) **Esterification**

Esters are obtained by refluxing the parent carboxylic acid with the appropriate alcohol with an acid catalyst.



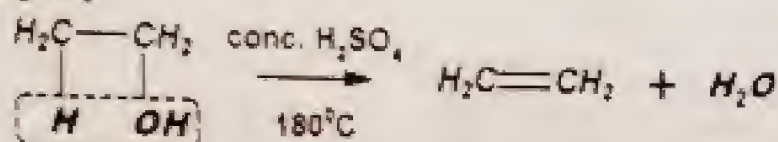
(iv) **Ether formation**





10. How does ethyl alcohol react with the following reagents?

(i) Conc.  $H_2SO_4$



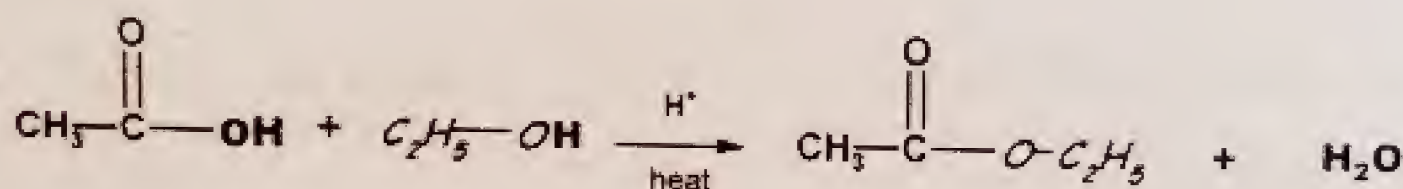
(ii) Na



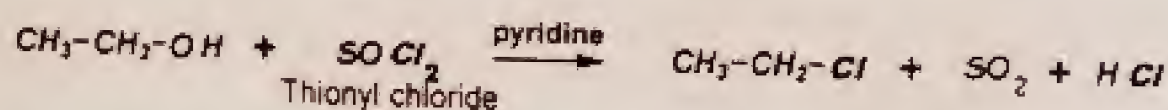
(iii)  $PCl_5$



(iv)  $CH_3COOH$



(v)  $SOCl_2$

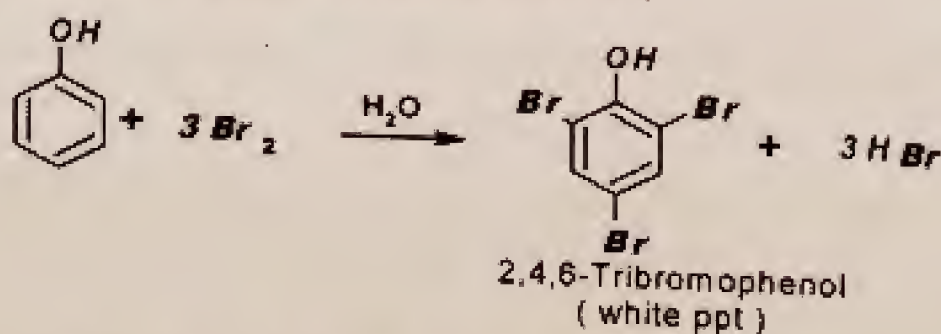


11. How will you distinguish between?

(i) an alcohol and a phenol

These can be distinguished by following ways

- Alcohol is neutral while phenol is acidic.
- Phenol gives white ppt with  $Br_2$  water while alcohol does not.



- Phenol gives deep purple colour with  $FeCl_3$  while alcohol does not.



(II) an alcohol and an ether

These can be distinguished by following test

Alcohols evolve  $H_2$  gas with Na metal while ether does not

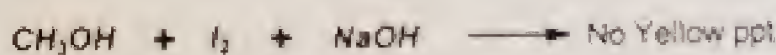
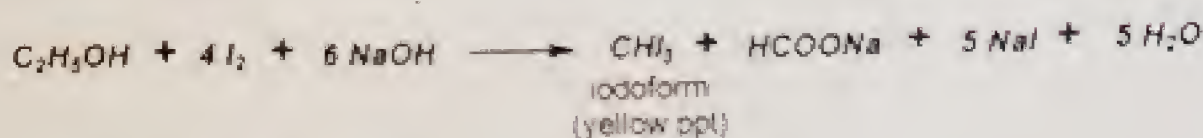


(iii) methanol and ethanol

These can be distinguished by iodoform test

Ethanol gives yellow ppt. of iodoform on reacting with NaOH and  $I_2$

Methanol does not give yellow ppt of iodoform with NaOH and  $I_2$



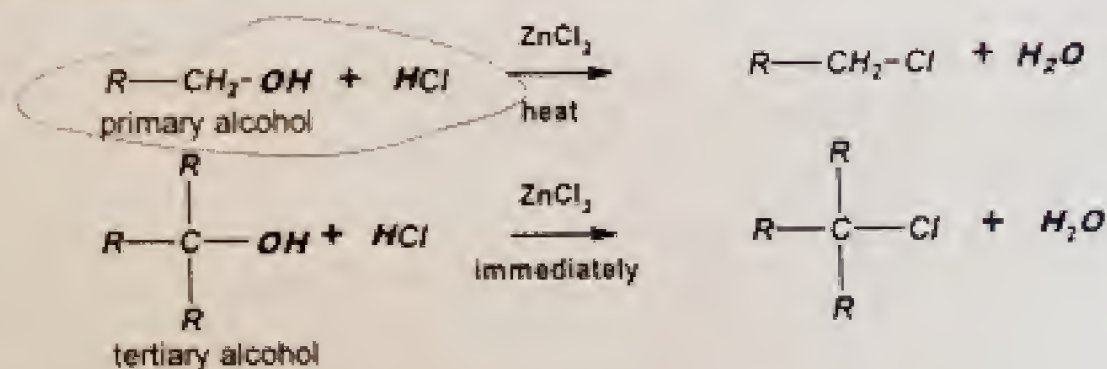
(iv) a tertiary alcohol and a primary alcohol

These can be distinguished by Lucas Test

When Lucas reagent ( $HCl + ZnCl_2$ ) is added to an alcohol,

Tertiary alcohol forms oily layer of alkyl halide immediately,

While primary alcohol forms oily layer only on heating

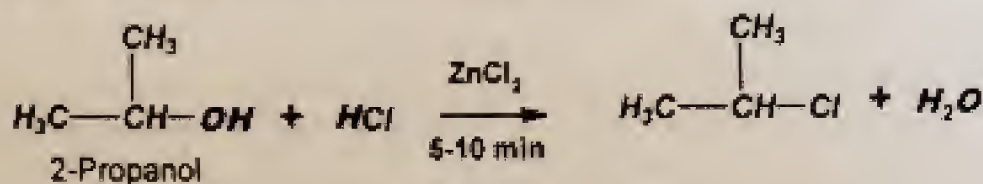


(v) 1-propanol and 2-propanol

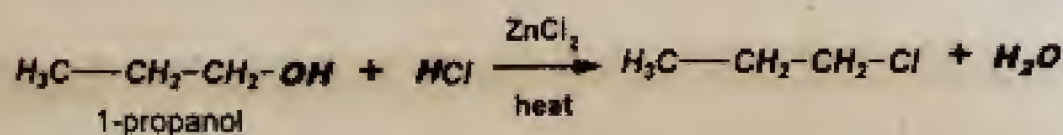
1-propanol is primary alcohol while 2-propanol is secondary alcohol. These can be distinguished by Lucas test

When Lucas reagent ( $HCl + ZnCl_2$ ) is added to an alcohol,

2-propanol forms oily layer of alkyl halide within 5 - 10 minutes,



While 1-propanol forms oily layer only on heating

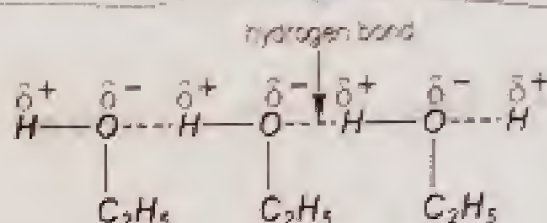




12. Give reason for the followings:

(i) Ethyl alcohol is a liquid while ethyl chloride is a gas.

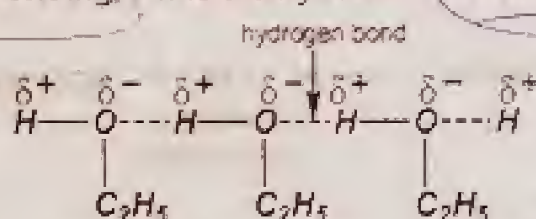
Ethyl chloride has weak dipole-dipole forces while ethanol has strong hydrogen bonding.



Due to strong H-bonding in ethanol, its molecules are tightly held together. Thus, ethanol is a liquid while ethyl chloride is gas.

(ii) Ethanol has higher boiling point than diethyl ether.

Ethanol has strong hydrogen bonding, while diethyl ether have weak van der waals' forces.



Due to strong H-bonding in ethanol, its molecules are tightly held together. Thus, it is difficult to boil ethanol than diethyl ether. Hence, ethanol has higher boiling point than diethyl ether.

(iii) Absolute alcohol cannot be prepared by fermentation process.

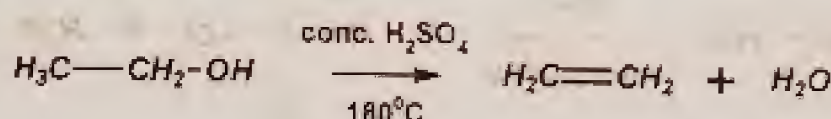
Absolute alcohol can not be obtained by fermentation process. It is because at higher conc. of alcohol enzyme of yeast becomes inactive and process stops.

Actually, alcohol obtained by fermentation process is only upto 12%. This alcohol is further concentrated by distillation to about 95% called rectified spirit. Rectified spirit is further distilled with lime to give absolute alcohol.

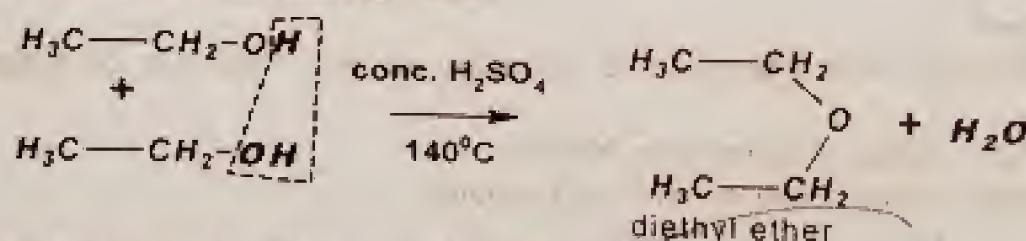
(iv) Ethanol gives different products with conc.  $H_2SO_4$  under different conditions.

Ethanol gives two types of product in different conditions.

High temperature, low alcohol conc.

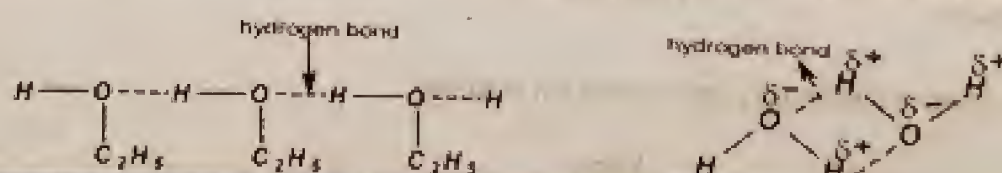


Low temperature, high alcohol conc.



(v) Water has higher boiling point than ethanol.

In water, two hydrogen bonds are formed per molecule while in ethanol only one hydrogen bond is formed per molecule. Thus due to extensive hydrogen bonding in  $H_2O$ , its boiling point is greater than ethanol.





**TEST YOUR SKILLS**

Marks: 85

**OBJECTIVE**

Marks: 17

20 Minutes

Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Circle the correct option i.e. A/B/C/D. Each part carries one mark.

Which one is the general formula for monohydric alcohols?

- A.  $C_nH_{2n}OH$  B.  $C_{n+1}H_{2n+1}OH$  C.  $C_{2n}H_{2n+2}OH$  D.  $C_nH_{2n+1}OH$

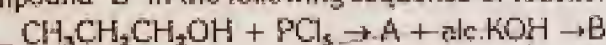
Rectified spirit contain alcohol at about

- A. 90% B. 100% C. 95% D. 85%

Fermentation of starch to give alcohol occurs mainly with the help of

- A.  $O_2$  B. Air C.  $CO_2$  D. Enzymes

The compound 'B' in the following sequence of reaction is



- A. Propyne B. Propene C. Propane D. Propanal

Phenol react with acetyl chloride in the presence of a base to form an?

- A. Acid B. Alcohol C. Citric acid D. Ester

An industrial method for preparation of methanol is

- A. Catalytic reduction of  $CO + 2H_2$  in the presence of  $ZnO-Cr_2O_3$   
B. By reacting methane with steam at  $900^\circ C$  with a Ni-catalyst  
C. By reducing  $HCHO$  with aqueous  $NaOH$  solution  
D. By reducing  $HCHO$  with  $LiAlH_4$  followed by hydrolysis

Ethanol is denatured by adding

- A. Methanol B. Acetone C. Propanol D. All of the above

Phenol is also known as

- A. Carboic acid B. Carbonic acid C. Carboxylic acid D. None

Alcohols of low molecular weight are

- A. Soluble in water B. Soluble in water on heating C. Insoluble in water D. Insoluble in all solvents

Methyl alcohol is not used

- A. as a solvent B. as an ant freezing agent  
C. as a substitute for petrol D. for denaturing of ethyl alcohol

When Phenol reacts with  $CH_3COCl$  the product formed is

- A. Ether B. Alcohol C. Aldehyde D. Ester

Williamsons synthesis of ethers is superior to alcohols because it makes

- A. Symmetrical ethers B. Asymmetrical ethers  
C. Either at room temperature D. Both symmetrical and asymmetrical ethers

Diphenyl ether is also called

- A. Phenoxy benzene B. Benzoxycobenzene C. Hexosybenzene D. Phenoxy ether

Hydrogen bonding is maximum in

- A. Ethanol B. Diethyl ether C. Ethyl chloride D. Triethyl amine

What is product in the following sequence of operations?

- Chlorobenzene +  $NaOH \rightarrow A + HNO_3$  (conc.)  $\rightarrow$  product  
A. o-nitrophenol B. p-nitrophenol C. both 'a' and 'b' D. picric acid

Which one of the following compounds does not contain carboxylic group

- A. Acetic acid B. Formic acid C. Picric acid D. Benzoic acid

(xvii) in a reaction  $C_6H_5-O-C_6H_5 + HI \rightarrow X$ , then X should be

- A.  $C_6H_5OH$  only B.  $C_6H_5I$  C.  $C_6H_5OH$  and  $C_6H_5I$  D. No reaction

**SUBJECTIVE**

Time: 2:35 Hours

Total Marks Section B and C: 68

**Section - B (Marks 42) (14 x 3 = 42)**

Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines.

There are different structural isomers of formula  $C_4H_9OH$ .

- a. Draw the structures of the four Alcohols of formula  $C_4H_9OH$  02  
b. Classify these isomers as primary, secondary or tertiary 01

Ethanol is prepared on industrial scale world over

- a. Name the process, temperature and enzymes used for the above process when ethanol is prepared from the residue of sugar with equations. 02  
b. Only 12% alcohol can be prepared by this process. Why? 01



CH # 18: Alcohols, Phenols and Ethers

- (i) a. What is Absolute alcohol and Rectified alcohol? 01  
b. Absolute alcohol can not be prepared by fermentation process. Why? 01  
c. What is meant by Denaturing of alcohol? 01
- (ii) Explain why- 1.5  
a. Hydroxyl group (-OH) in phenol is ortho-para directing 1.5  
b. Phenol undergoes Nitration faster than nitrobenzene.
- (iii) a. Absolute alcohol can not be prepared by fermentation of molasses. Give reason. 1.5  
b. How is alcohol denatured? 1.5
- (iv) a. Why is Ethane a gas but Ethanol a liquid? 01  
b. Why does the solubility of higher alcohol decrease in water? 01  
c. Why does phenol show acidic nature? 01
- (v) Ethers contain  $\text{—O—O—O—}$  functional group.  
a. Describe preparation of Ethers by Williamson's Synthesis. 1.5  
b. Why are Ethers slightly soluble in water? 1.5
- (vi) a. What is difference between alcohols and phenols? 01  
b. What are monohydric and polyhydric alcohols? 01  
c. Write structures of iso-butyl alcohol and sec-butyl alcohol. 01
- (vii) How ethanol is prepared from starch? Write all balanced equations and conditions. 03
- (viii) a. What is rectified spirit? 01  
b. How rectified spirit may be converted into absolute alcohol? 02
- (ix) a. Why lower alcohols are soluble in water? 1.5  
b. Why melting and boiling points of alcohols are higher than corresponding alkanes? 1.5
- (x) Alcohols give variety of reactions  
a. During reactions of alcohols, under which conditions C-O bond breaks. 1.5  
b. Under which conditions O-H bond breaks during reactions of alcohols. 1.5
- (xi) a. Why tertiary alcohols are resistant towards oxidation? 01  
b. Alcohols react with  $\text{H}_2\text{SO}_4$  to give different products at different temperature. Give equations. 02
- (xii) a. What is Lucas reagent? How will you differentiate between 1-propanol and 2-propanol by this reagent. 02  
b. What is Dow's process? 01
- (xiii) a. How will you differentiate between methanol and ethanol. 01  
b. Write down the structural formulas of (i) Carbolic-Acid (ii) Picric Acid 01  
c. Give two uses of methyl alcohol. 01
- (xiv) a. Write IUPAC names of the following compounds: A.  $(\text{CH}_3)_2\text{CH OH}$  B.  $(\text{CH}_3)_2\text{CH CH}_2\text{ OH}$  02  
b. How will you obtain phenol from benzenesulphonic acid? 01
- (xv) a. Alcohols and phenols both have OH group but phenols are more acidic than alcohols. 02  
b. Give one reaction of phenol in which it acts as an acid. 01
- (xvi) a. Prepare benzene and picric acid from phenol? 01  
b. How will you differentiate between an alcohol and phenol? 01  
c. Water has higher b.p than alcohols. Why? 01
- (xvii) a. How will you obtain bakelite from phenol? 1.5  
b. Ethyl alcohol is a liquid while methyl chloride is a gas. 1.5



Section – C

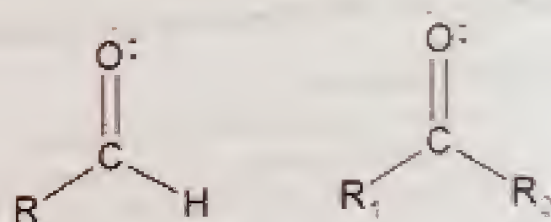
Attempt any TWO questions. All questions carry equal marks. ( $2 \times 13 = 26$ )

- Q. 3. (a) What happens when 04  
 (i) Phenol is treated with acetyl chloride  
 (ii) Ethanol is reacted with ethyl magnesium bromide  
 (iii) Diethyl ether is reacted with  $\text{PCl}_5$   
 (iv) Ethyl bromide is heated with silver oxide  
 (b) Give IUPAC names and structures of the following compounds. 05  
 (i) sec-butyl alcohol (ii) Lactic acid  
 (iii) ter-butyl alcohol (iv) Tartaric acid (v) Diphenyl ether  
 c. What is an Esterification reaction. 02  
 d. What are simple and mixed ethers? 02
- Q. 4. a. Show by reaction and diagram the industrial preparation of Methanol. 03  
 b. How does phenol reacts with 04  
 (i)  $\text{HNO}_3$  (ii)  $\text{H}_2\text{SO}_4$  (iii)  $\text{H}_2/\text{Ni}$  (iv)  $\text{NaOH}$   
 c. How does methanol reacts with 04  
 (i)  $\text{SOCl}_2$  (ii)  $\text{PCl}_5$  (iii)  $\text{NH}_3$  (iv)  $\text{CH}_3\text{COCl}$   
 d. Give four uses of phenol. 02
- Q. 9. a. Explain hydrogen bonding in alcohols, phenols and ethers? 03  
 b. What is oxonium ion? How it can be generated from ethers? 03  
 c. How may alcohols be oxidized? 03  
 d. Carry out the following conversions 04  
 (i) Benzene to cyclohexanol (ii) Ethanol to ethyl iodide



## CHAPTER # 19

# ALDEHYDES AND KETONES

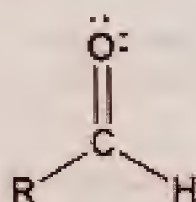


## INTRODUCTION

Organic compounds containing the carbonyl functional group are called aldehydes and ketones.

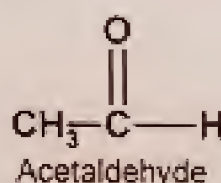
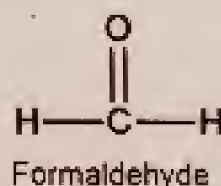
### ALDEHYDES

**Functional Group:** In aldehydes, the C-atom of carbonyl group is directly attached to at least One H-atom.  
**Structure Formula:** An aldehyde may be represented by the general formula structure



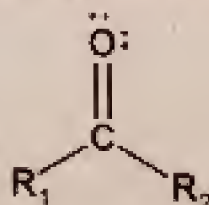
**General Formula:** The homologous series of aldehydes have general formula  $\text{C}_n\text{H}_{2n}\text{O}$ .  
**Occurrence:** Aldehyde groups are present in most sugars. They are the principal constituents of a number of essential oils used as fragrances and flavors.

**Examples:**



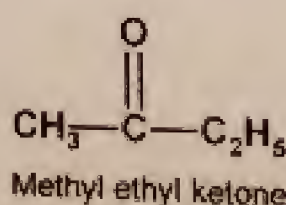
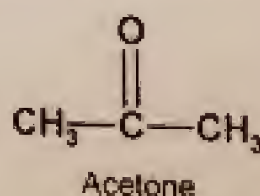
### KETONES

**Functional Group:** In ketones, the C-atom of carbonyl group is bonded to two carbon atoms called ketonic group.  
**Structure Formula:** A ketone may be represented by the general formula structure



**General Formula:** The homologous series of ketones have general formula  $\text{C}_n\text{H}_{2n}\text{O}$ .  
**Occurrence:** Ketonic group is present in camphor and fructose.

**Examples:**



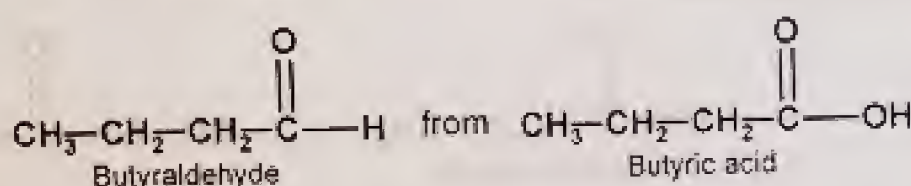
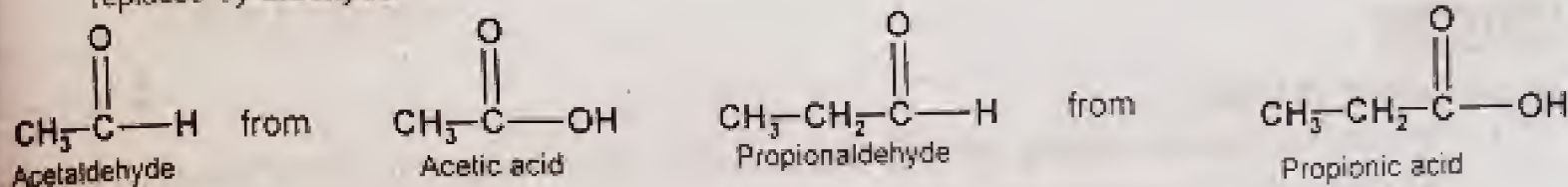


## NOMENCLATURE:

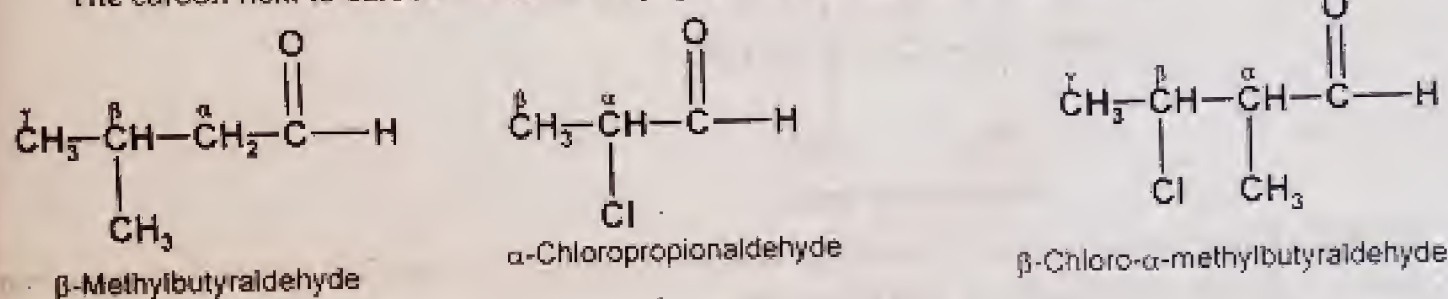
### ALDEHYDES

#### (a) COMMON NAMES:

- An aldehydes is named after the name of carboxylic acid obtained on its oxidation, the ending **-ic acid** is replaced by **aldehyde**.



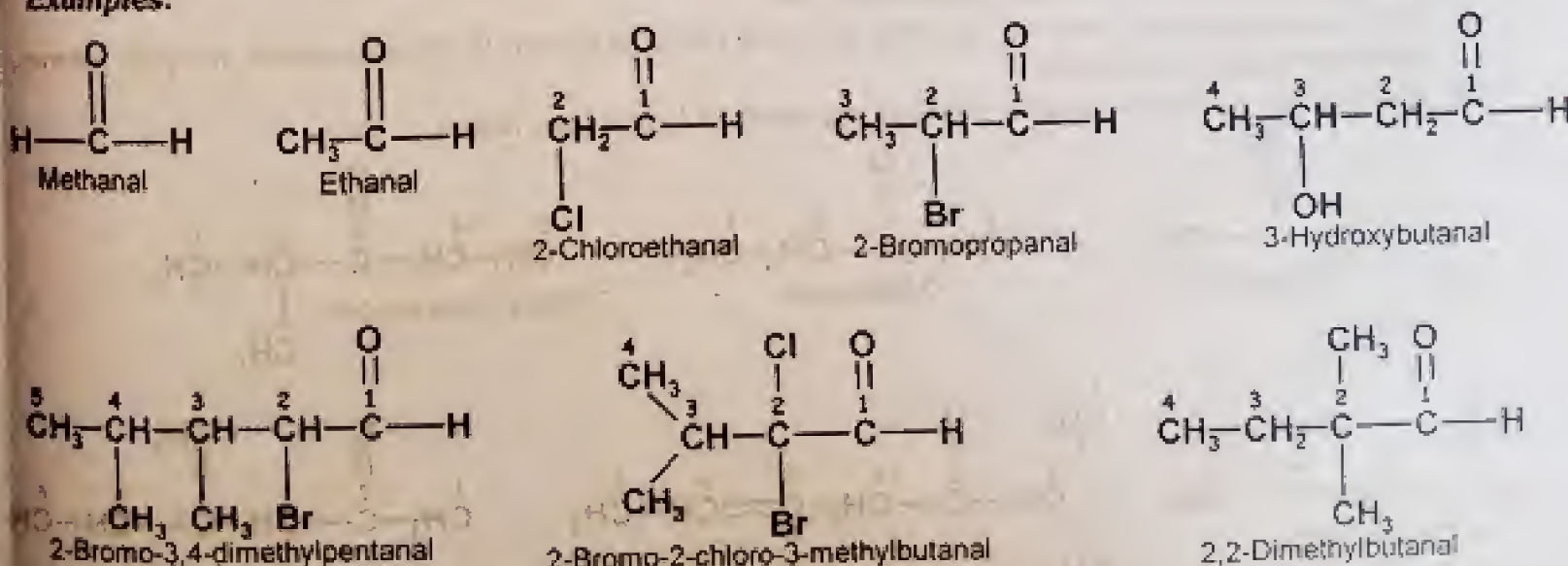
- For naming substituted aldehyde, the chain is labeled by using  $\alpha, \beta, \gamma \dots$  etc. The carbon next to carbon of the carbonyl group is indicated by ' $\alpha$ ' and so on.



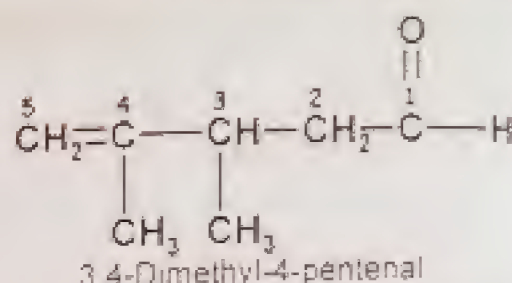
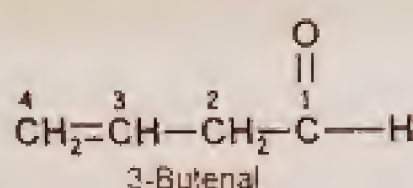
#### (b) IUPAC NAMES:

- The longest carbon chain containing the aldehydic group is taken as the parent hydrocarbon.
- The ending **e** of the alkane is replaced by **al**.
- The numbering starts from the carbon atom of the carbonyl group. The carbon atom of aldehydic group is always carbon number 1.
- The position of the substituent is indicated by numbers which is written before their number.

#### Examples:



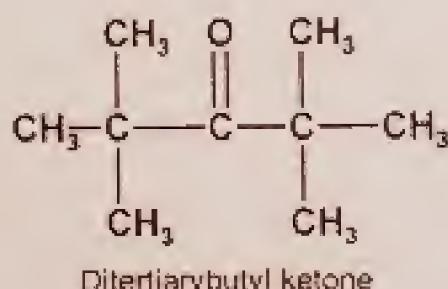
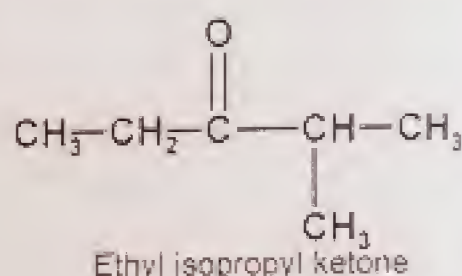
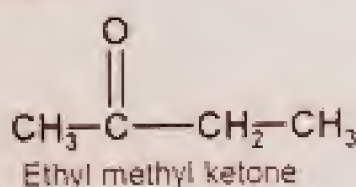
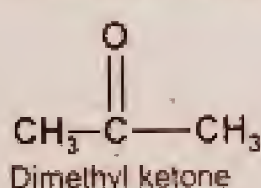




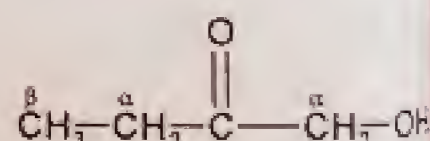
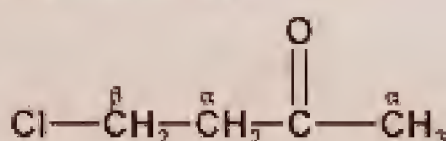
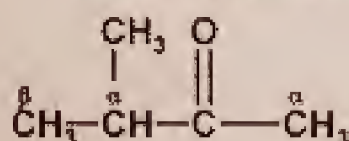
## KETONES

### (a) COMMON NAMES:

- Ketones are named by adding the word ketone after writing the names of alkyl or aryl group linked to the carbonyl carbon in alphabetical order.

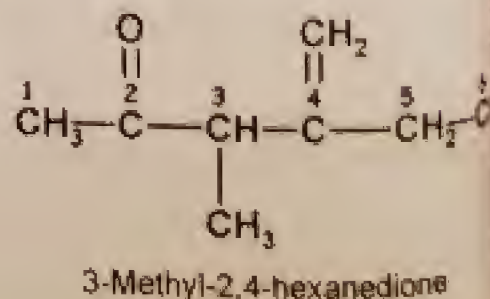
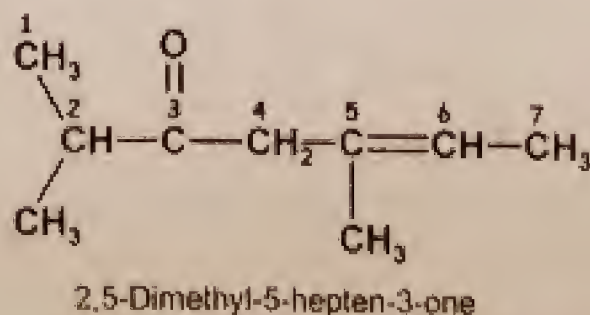
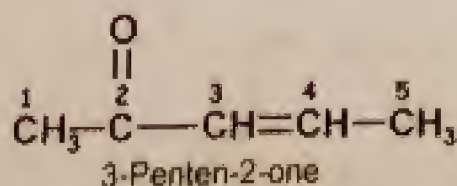
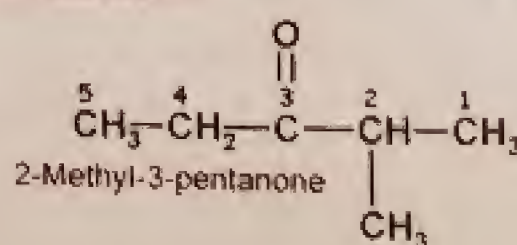
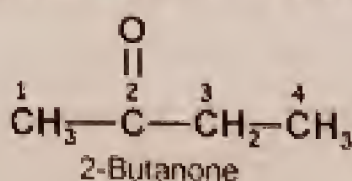
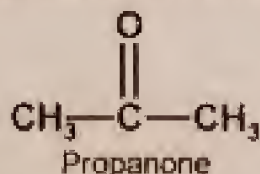


- Substituted ketones are named by labeling the chain using  $\alpha$ ,  $\beta$ ,  $\gamma$  ... etc. The carbon next to the carbonyl group is indicated by ' $\alpha$ ' and so on, e.g.

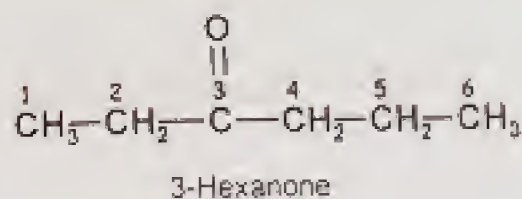
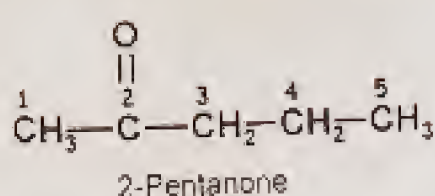
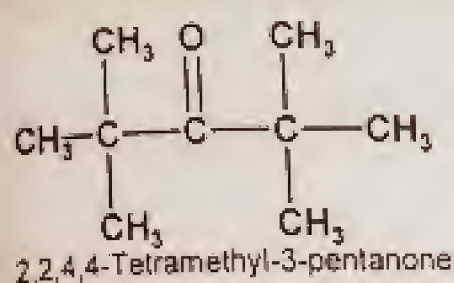


### (b) IUPAC NAMES:

- The longest chain containing the carbonyl group is taken as parent hydrocarbon.
- The ending e of hydrocarbon is replaced by one.
- The numbering starts from the end that gives the carbonyl carbon the lower number. In cyclic ketones, the carbonyl carbon is number 1.
- The positions of substituents are indicated by numbers before their names.



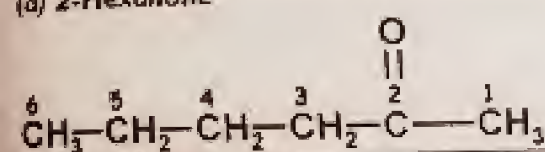




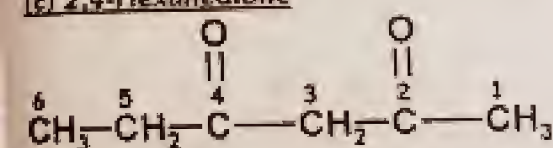
## QUICK QUIZ-1

(i) Write the structures of the following compounds:

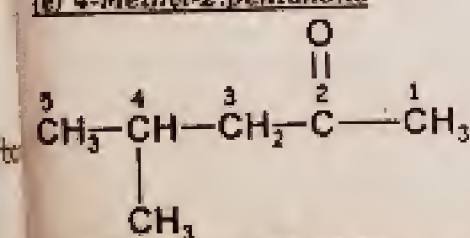
(a) 2-Hexanone



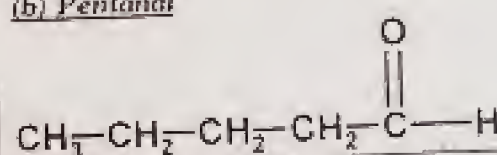
(c) 2,4-Hexanedione



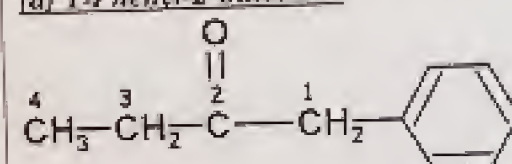
(e) 4-Methyl-2-pentanone



(b) Pentanal



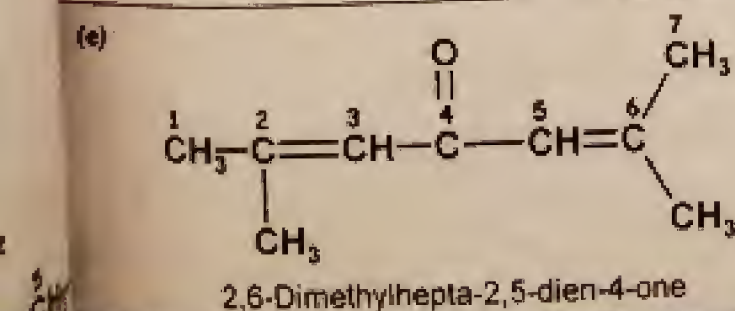
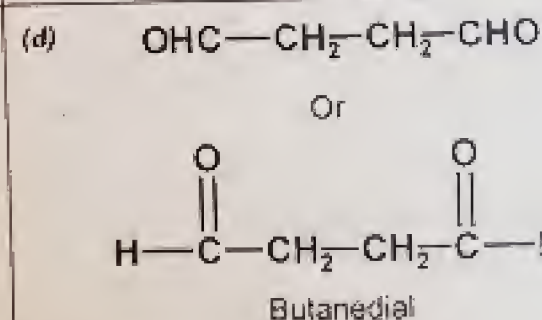
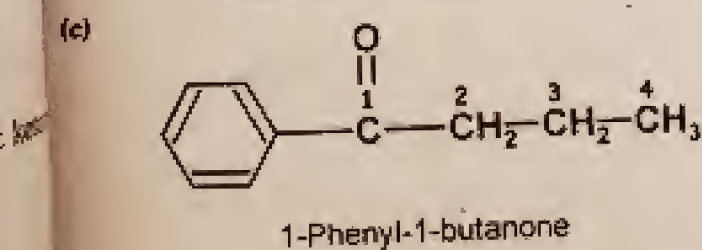
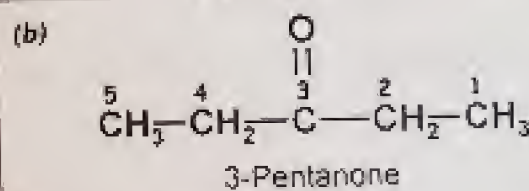
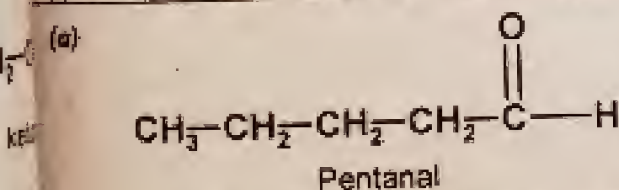
(d) 1-Phenyl-2-butanone



(f) 1-Phenyl-3-(2-methoxy phenyl)-1,3-propanedione

Incorrect Name: There is no propanedione

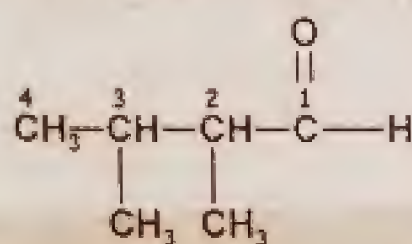
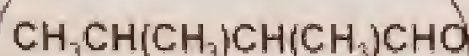
(i) Give the IUPAC names of the followings:



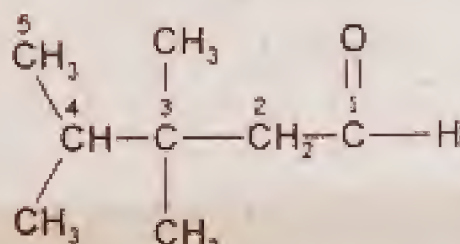


**MORE PRACTICE**

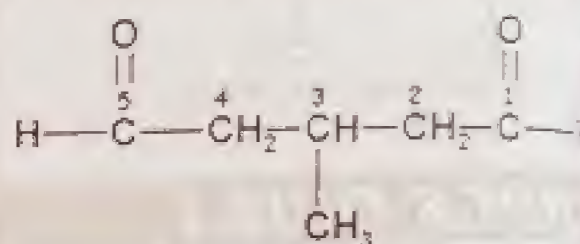
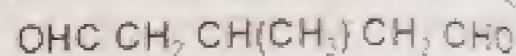
**ALDEHYDES**



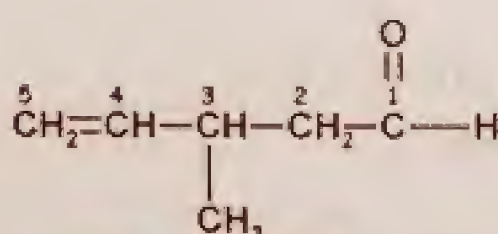
2,3-Dimethylbutanal



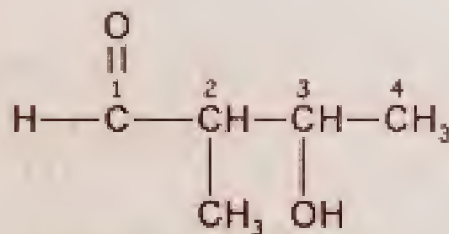
3,3,4-Trimethylpentanal



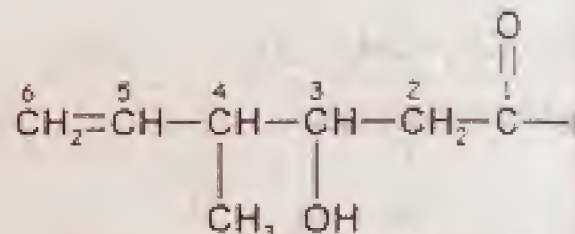
3-Methylpentanedial



3-Methyl-4-pentenal

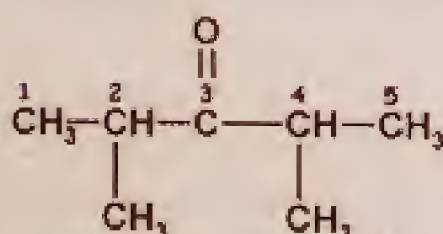


3-Hydroxy-2-methylbutanal

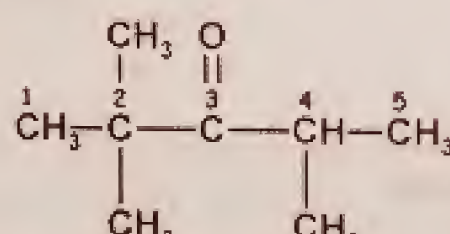


3-Hydroxy-4-methyl-5-hexenal

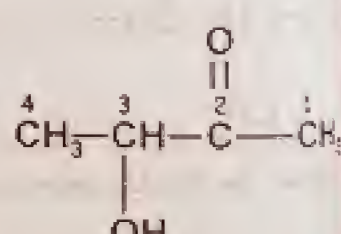
**KETONES**



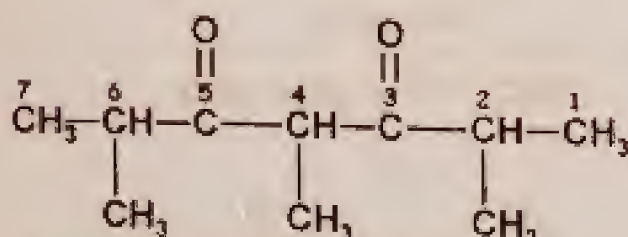
2,4-Dimethyl-3-pentanone



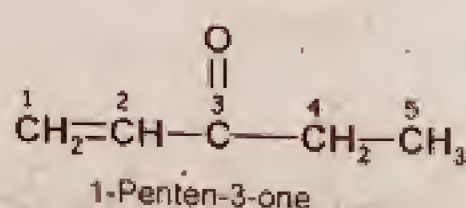
2,2,4-Trimethyl-3-pentanone



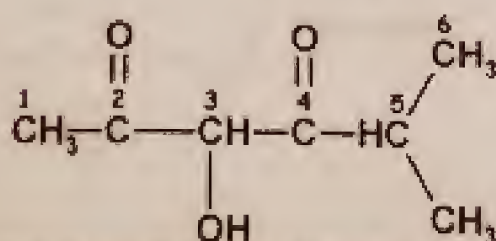
3-Hydroxy-2-butanone



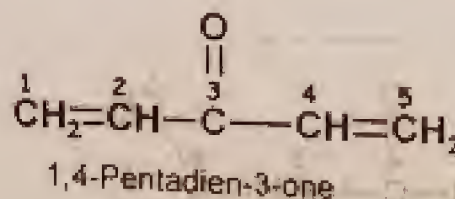
2,4,6-Trimethyl-3,5-heptanedione



1-Penten-3-one



3-Hydroxy-5-methyl-2,4-hexanedione



1,4-Pentadien-3-one



## PHYSICAL PROPERTIES

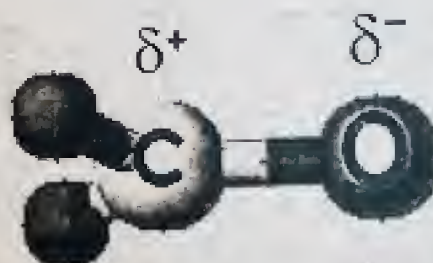
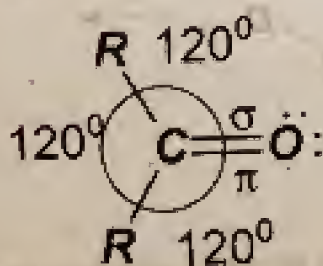
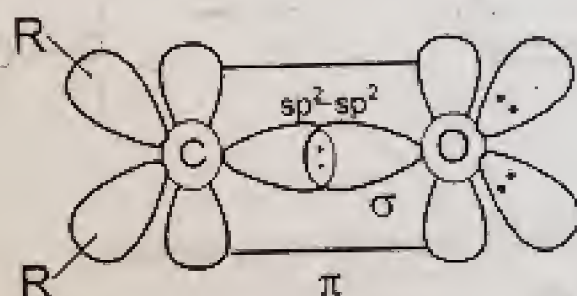
- The  $C=O$  bond has polar nature due to the electronegativity difference of the atoms.
- The polar nature of the  $C=O$  means that dipole-dipole interactions will occur.
- The  $C=O$  bonds cannot form hydrogen-bond with each other. However, the  $C=O$  can accept hydrogen bonds from hydrogen bond donors (e.g. water, alcohols).

The results of these effects are:

- higher melting and boiling points compared to analogous alkanes
- lower boiling points than analogous alcohols
- more soluble than alkanes but less soluble than alcohols in aqueous media

## STRUCTURE

- The carbonyl group consists of an O atom bonded to a C atom via a double bond.
- In carbonyl group both carbon and oxygen are  $sp^2$  – hybridized.
- A sigma bond is formed between C and O by the overlap of  $sp^2$  hybrid orbitals of C & O.
- Two lone pairs of oxygen are present in two  $sp^2$  hybrid orbitals, while carbon uses its two  $sp^2$  hybrid orbitals to form bond with other groups like alkyl groups (R).
- Both C and O contain one unhybridized p – orbital each, which overlap sideways to form a pi-bond.
- Three groups attached to the carbonyl carbon lie in same plane with bond angles of approximately  $120^\circ$ .



- Electron density between C and O is not equally shared.
- Oxygen due to its greater electronegativity, attracts charged cloud more towards itself. As a result O acquires  $\delta^-$  charge and C acquires  $\delta^+$  charge. Thus carbonyl group becomes polar.



## PREPARATIONS OF ALDEHYDES AND KETONES

### (1) OZONOLYSIS OF ALKENES

The alkenes are cleaved by ozone to give carbonyl compounds



**Reaction type:** Electrophilic Addition

- **Overall transformation:**  $\text{C}=\text{C}$  to two  $\text{C}=\text{O}$
- **Reagents:** Ozone,  $\text{O}_3$ , followed by a reducing work-up, usually  $\text{Zn}$  in acetic acid.
- It is convenient to view the process as cleaving the alkene into two carbonyl compounds.
- The substituents on the  $\text{C}=\text{O}$  depend on the substituents on the  $\text{C}=\text{C}$ .

#### MECHANISM:

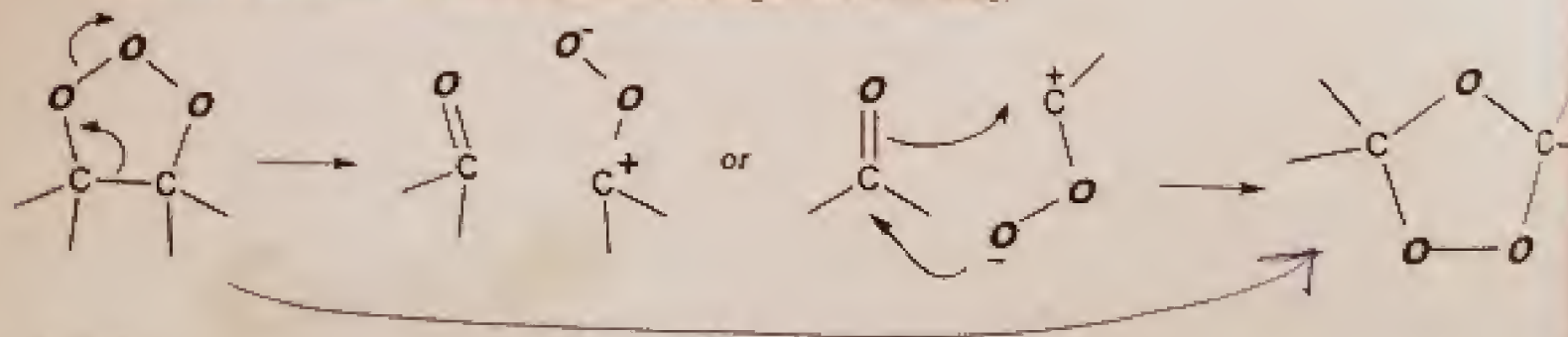
##### Step 1:

The  $\pi$ -electrons act as the nucleophile, attacking the ozone at the electrophilic terminal O. A second C-O is formed by the nucleophilic O attacking the other end of the  $\text{C}=\text{C}$ .



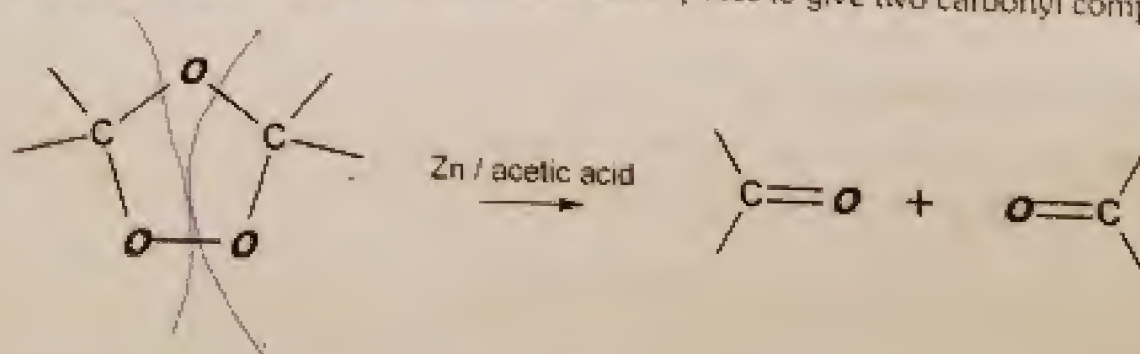
##### Step 2:

The cyclic species called the molozonide rearranges to the ozonide.



##### Step 3:

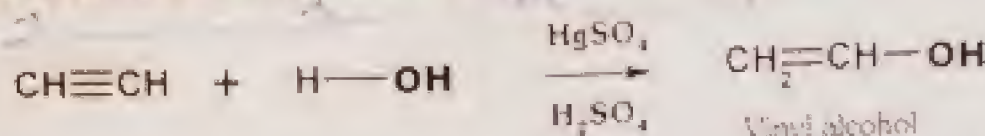
On work-up (usually  $\text{Zn}$  / acetic acid) the malozonide decomposes to give two carbonyl compounds.



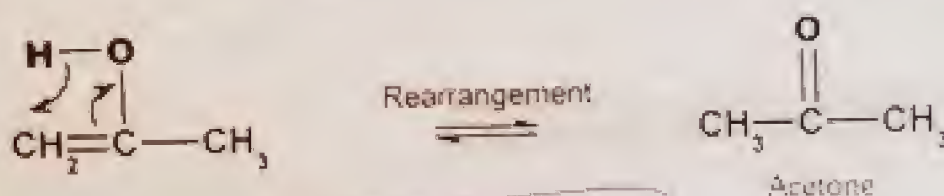
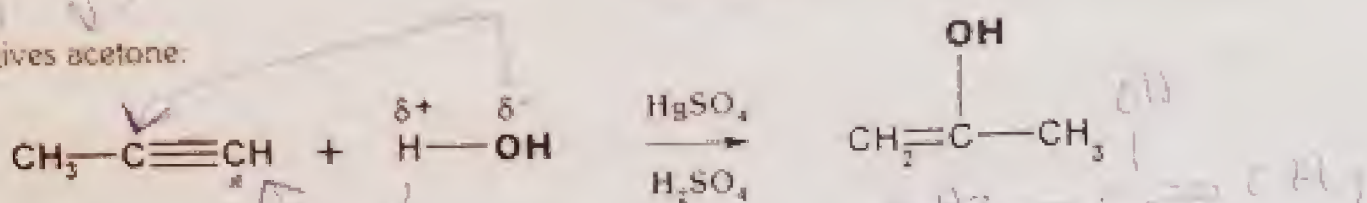


## (2) HYDRATION OF ALKYNES

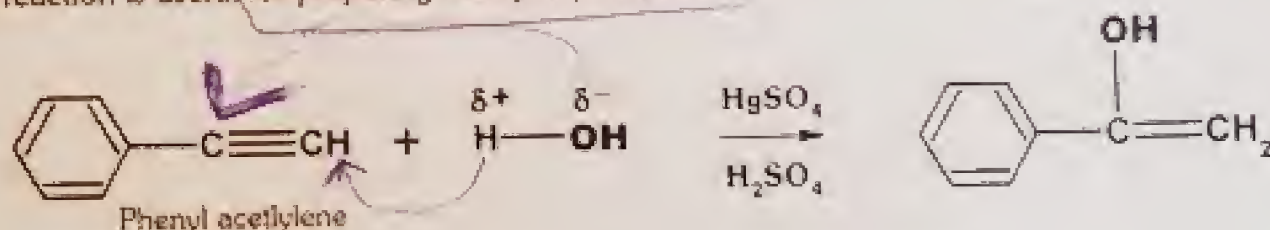
- Water adds on to alkynes in the presence of dil.  $\text{H}_2\text{SO}_4$  and  $\text{HgSO}_4$  to produce an aldehyde or ketone
- Enol forms as intermediate which isomerizes into aldehydes or ketones



- Propyne gives acetone:

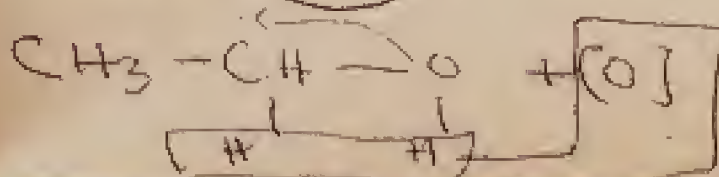
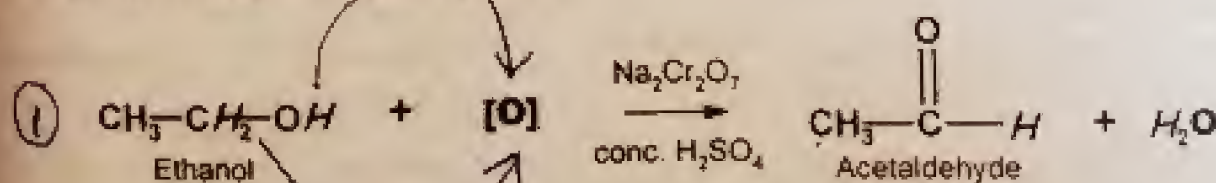


- This reaction is useful for preparing methyl aryl ketones

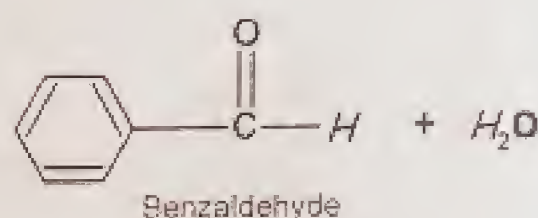
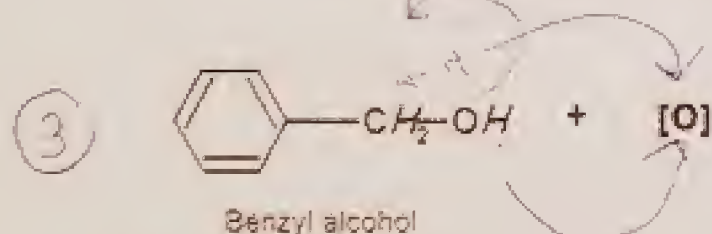
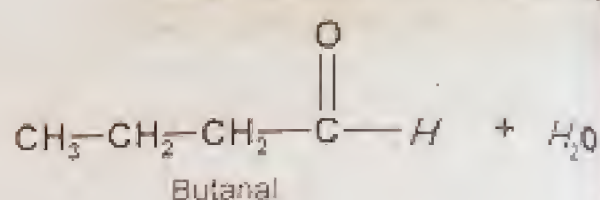
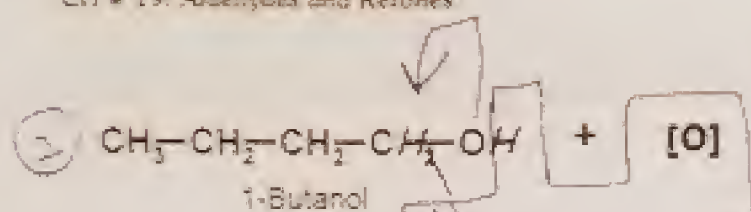


## (3) OXIDATION OF PRIMARY AND SECONDARY ALCOHOLS

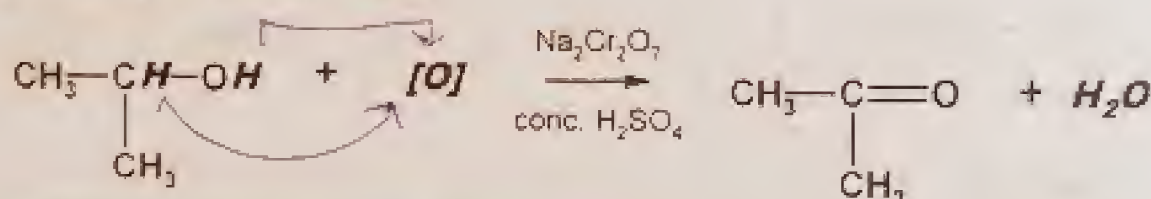
- Primary alcohols are oxidized to aldehydes by
  - warming with acidic dichromate solution or
  - Jone reagent ( $\text{CrO}_3 + \text{dil. H}_2\text{SO}_4 + \text{acetone}$ ) or
  - Sarett reagent ( $\text{CrO}_5$  in pyridine)





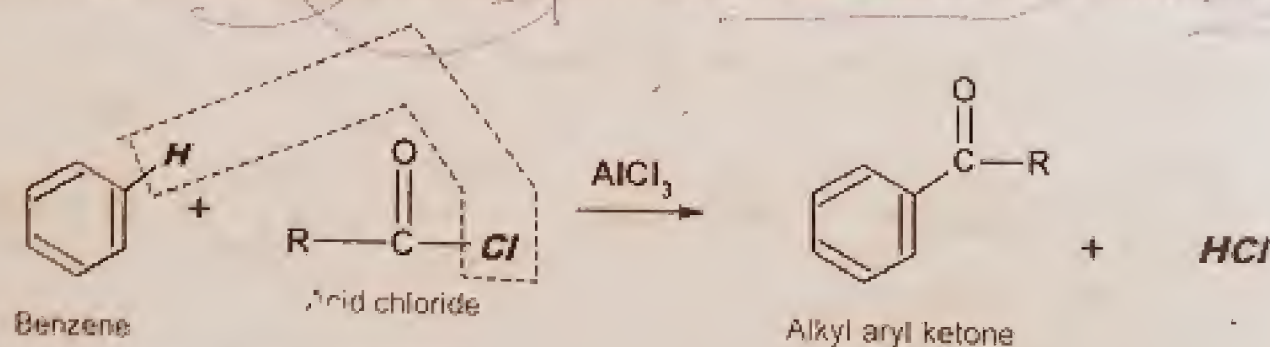


- Non-aqueous solvents are employed to avoid further oxidation.
- Secondary alcohols are oxidized to ketones.



#### (4) FRIEDEL-CRAFTS ACYLATION OF BENZENE

- It is the substitution of acyl group in an organic compound in the presence of  $\text{AlCl}_3$  or some other Lewis acid.

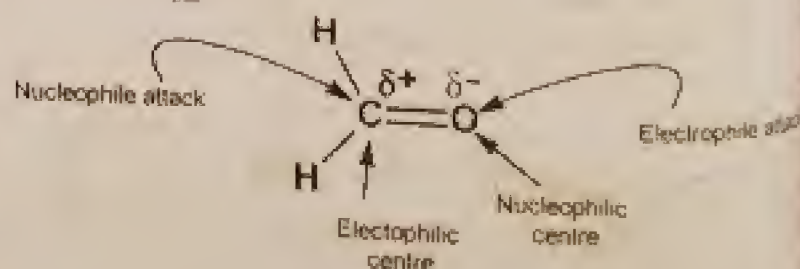


- $\text{AlCl}_3$  generates acylium ion ( $\text{R---C}^+=\text{O}$ , electrophile) which is substituted in the aromatic ring.

Exercise Q3 (i) What is the reactivity of the carbonyl group?

#### REACTIVITY

- The double bond of the carbonyl group has a  $\sigma$ -bond and a  $\pi$ -bond.
- As oxygen is more electronegative, it attracts the  $\pi$ -electrons to itself. This attraction makes the carbonyl group a polar group.
- The oxygen atom has a partial negative charge on it and the carbon atom has partial positive charge.
- Hence, it makes oxygen atom nucleophile and carbon atom becomes electrophile.

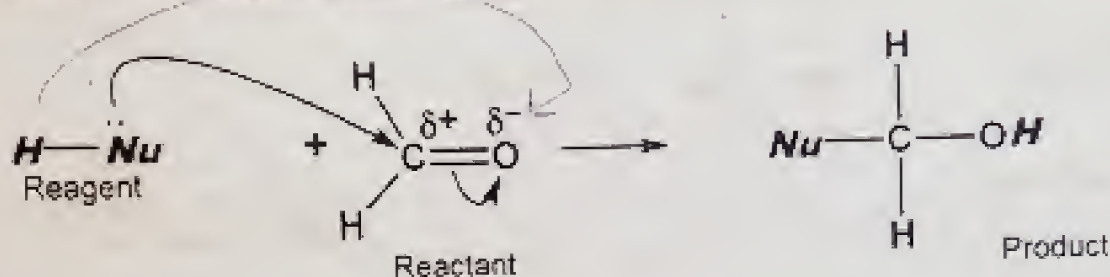




## REACTIONS OF ALDEHYDES AND KETONES

### NUCLEOPHILIC ADDITION

The general reaction of nucleophilic addition is given below.



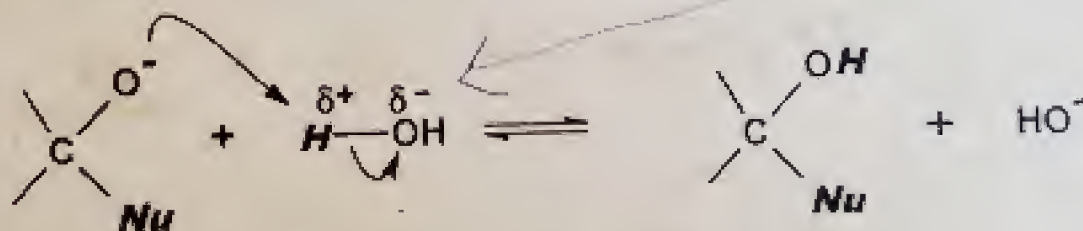
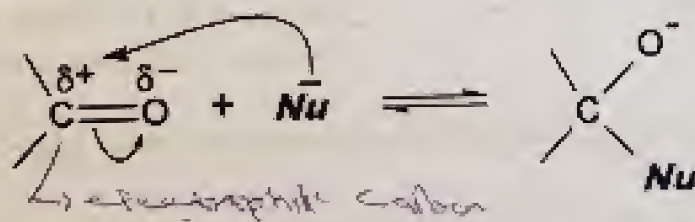
There are two types of nucleophilic addition reactions of carbonyl compounds.

- (i) Base catalysed nucleophilic addition reaction
- (ii) Acid catalysed nucleophilic addition reaction

#### (i) BASE CATALYSED

- A base catalysed nucleophilic addition reaction takes place with a strong nucleophilic reagent.
- The base reacts with the reagent and generates the nucleophile.
- The addition is initiated by the attack of a nucleophile on the electrophilic carbon of the carbonyl group.

#### GENERAL MECHANISM



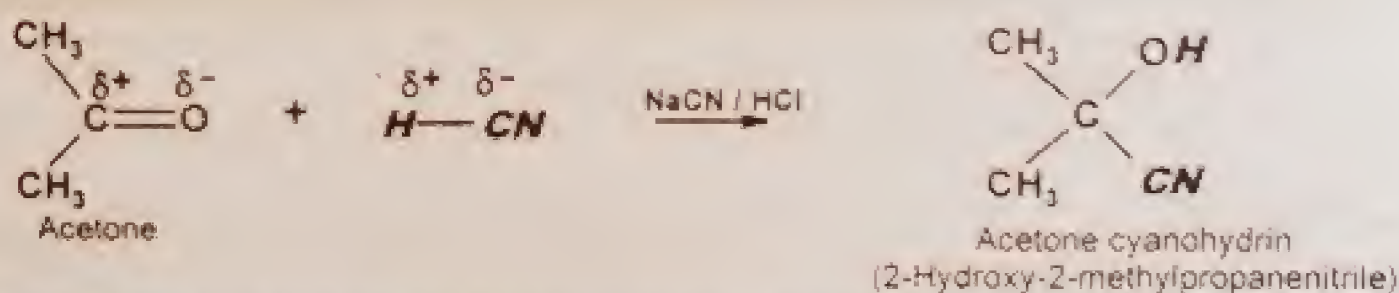
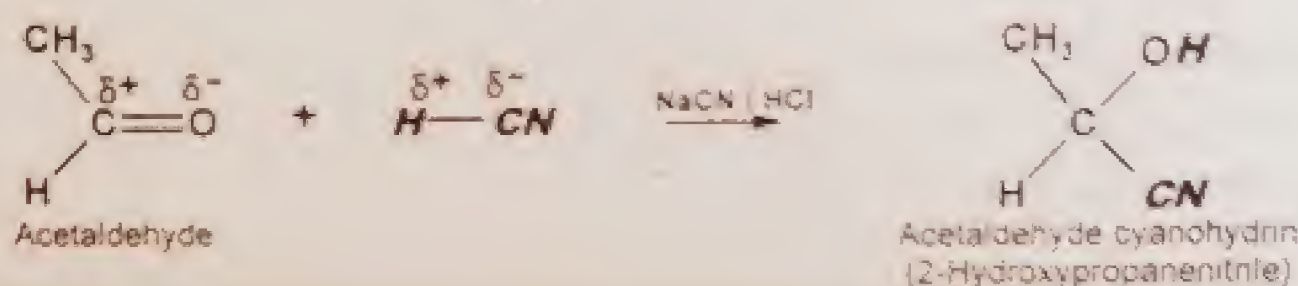
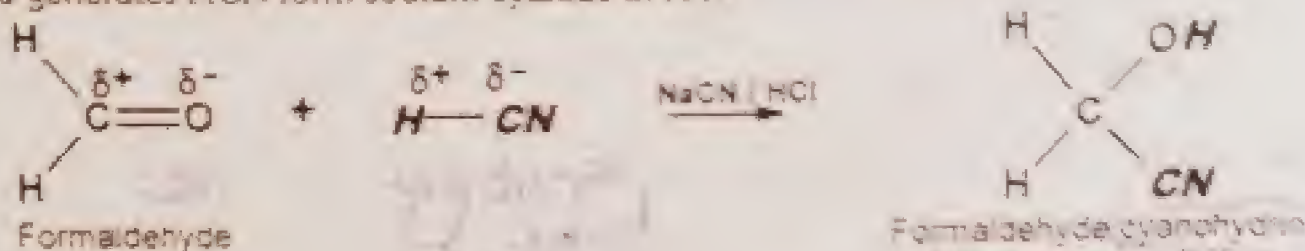
There are five types of base catalysed nucleophilic addition reactions of carbonyl compounds.

- (1) Addition of hydrogen cyanide
- (2) Addition of Grignard's reagent
- (3) Addition of sodium bisulphate
- (4) Condensation reactions
- (5) Haloform reactions

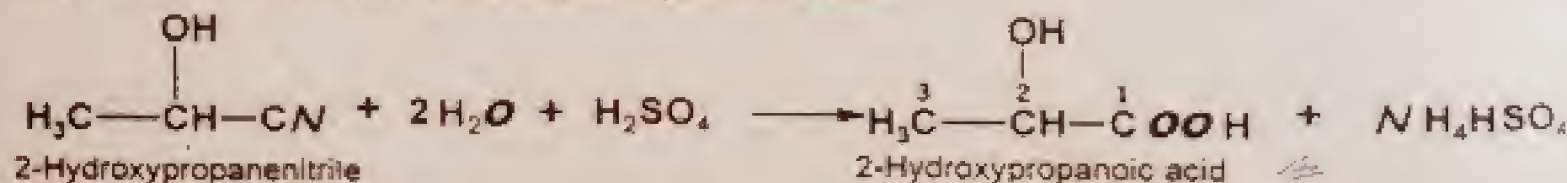


## 11. ADDITION OF HYDROGEN CYANIDE

- Hydrogen cyanide adds to aldehydes and ketones to form cyanohydrins.
- The acid generates HCN from sodium cyanide in HCl.



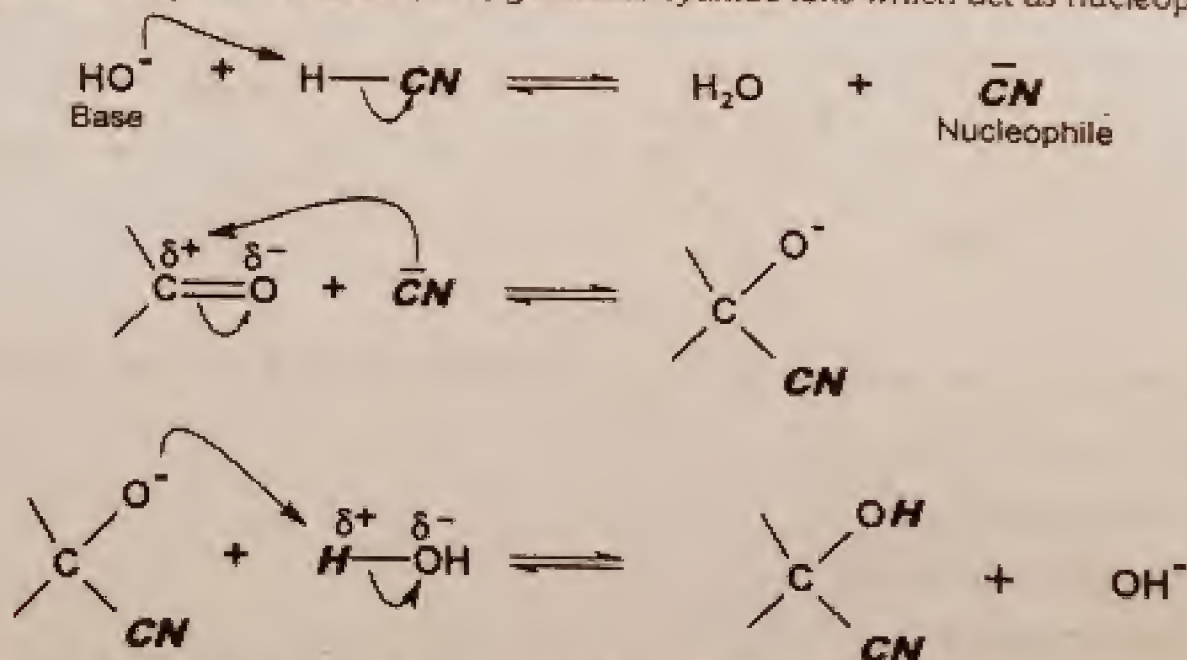
- The reaction is used in the synthesis of  $\alpha$ -hydroxyl acid. These acids contain one carbon atom more than the number of carbon atoms in the starting aldehydes or ketones.



**Exercise Q2 (III) What is the mechanism of HCN addition to carbonyl compounds?**

### Mechanism

The reaction is base catalysed. The base ( $\text{OH}^-$ ) generates cyanide ions which act as nucleophile.



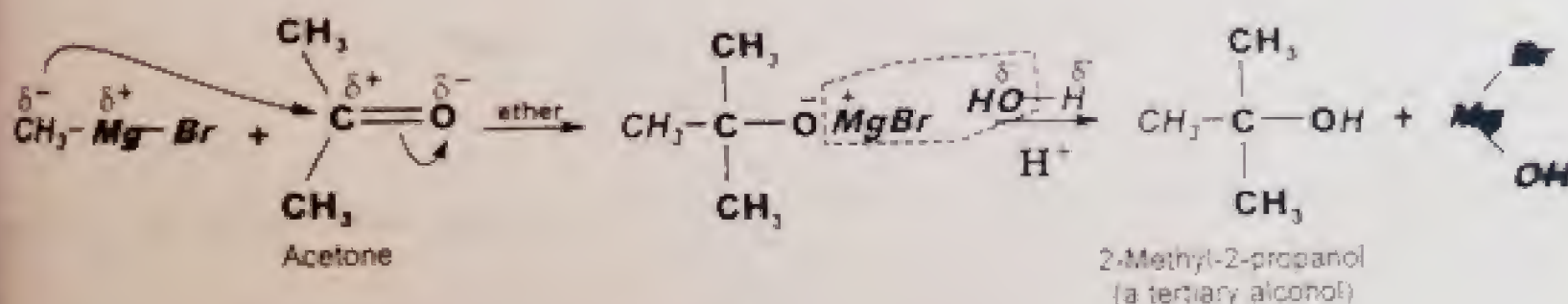
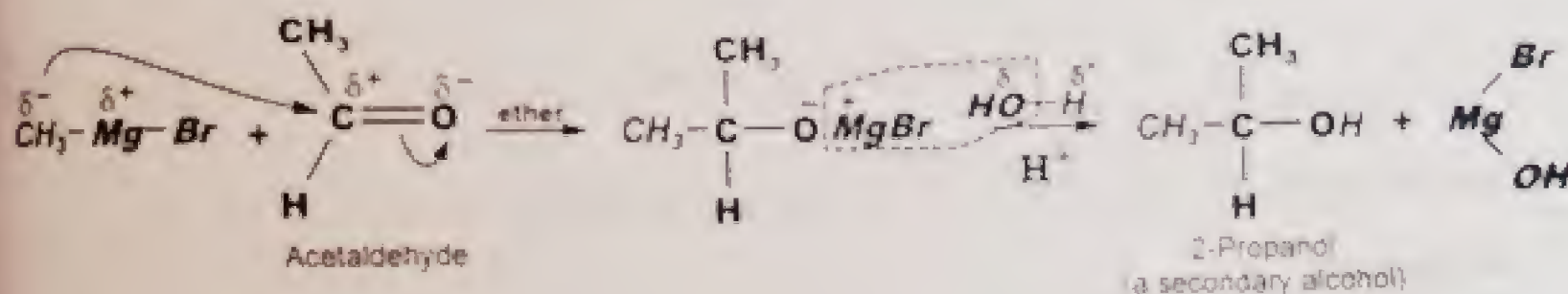
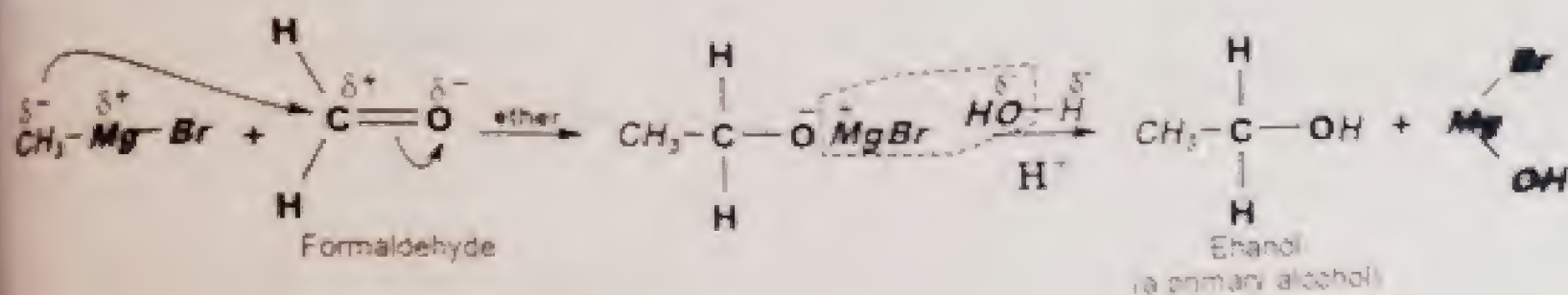
The hydroxide ion liberated reacts with undissociated hydrogen cyanide. Thus, it produces more cyanide ions, which in turn react with more carbonyl compound.



Exercise Q2 (e) What is the addition product of Grignard reagent to formaldehyde, acetaldehyde and ketone?

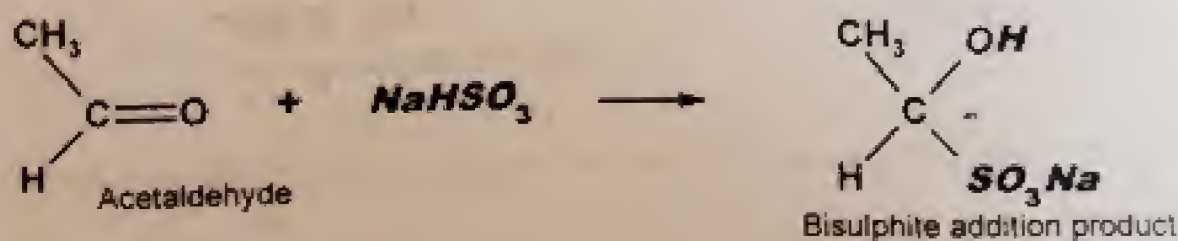
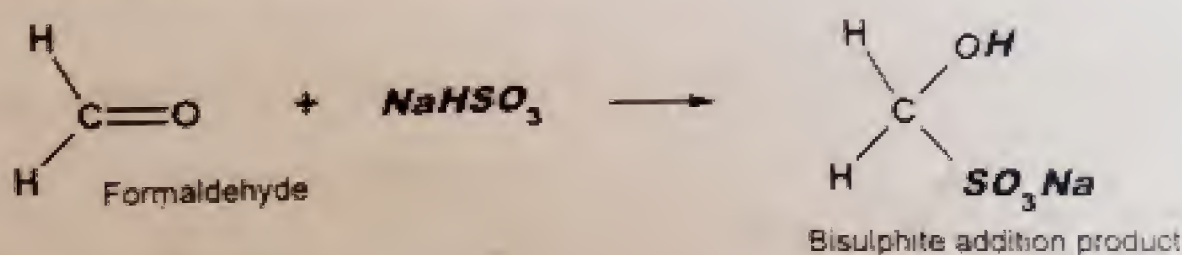
## 2) ADDITION OF GRIGNARD'S REAGENT

Grignard's reagents add to aldehydes and ketones to form adduct (addition product) which on hydrolysis with a dilute mineral acid give alcohols.

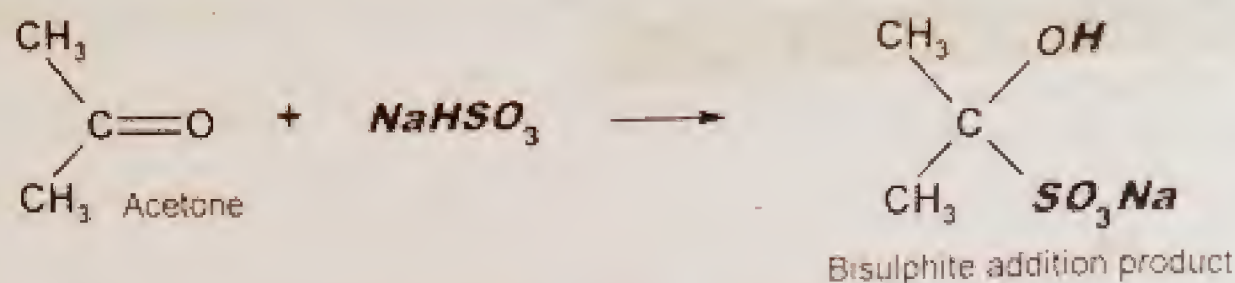


## 3) ADDITION OF SODIUM BISULPHATE

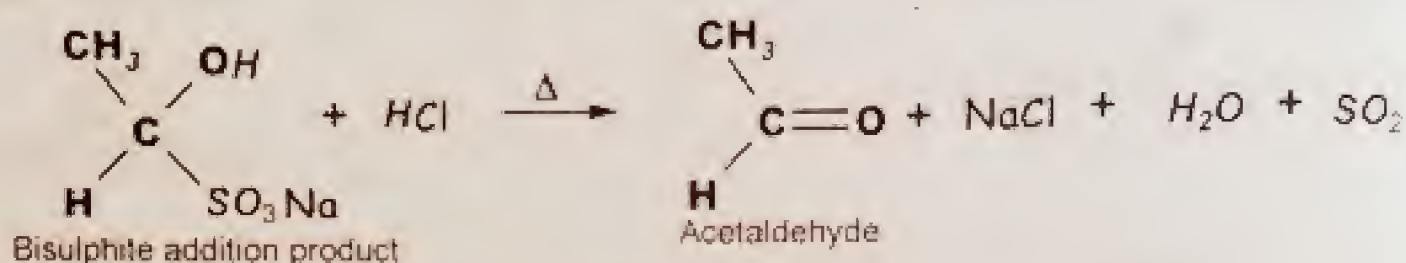
- Aldehydes and small methyl ketones react with a saturated aqueous solution of sodium bisulphate to form a crystalline white precipitate of sodium bisulphate adduct.







- Bisulphite on heating a dilute mineral acid (HCl or H<sub>2</sub>SO<sub>4</sub>) regenerates the parent aldehydes or ketone.

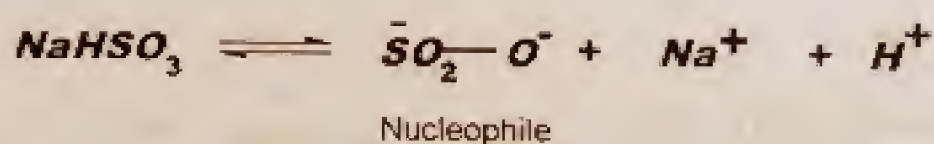


- The reaction is used for the separation and purification of carbonyl compounds from non-carbonyl compounds such as alcohols.

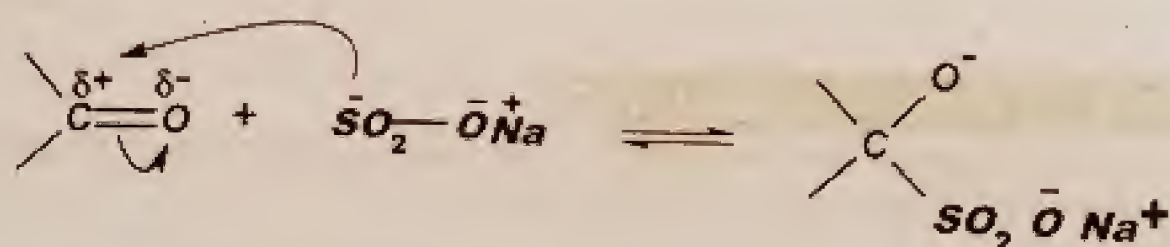
**Exercise Q2 (x)** Give the mechanism of addition of sodium bisulphate to ketones.

#### Mechanism

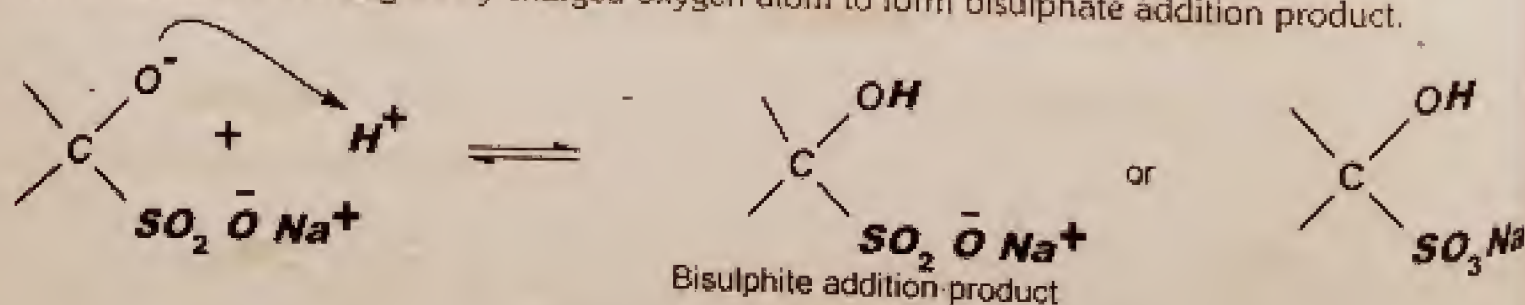
- Sodium bisulphate ionizes to form sulphate ions.



- The sulphite ion acts as a nucleophile, since the sulphur atom is more nucleophilic than oxygen, a C-S bond is formed.



- Proton is attached to the negatively charged oxygen atom to form bisulphite addition product.



- Ketones in which both alkyl groups are larger than methyl do not react with sodium bisulphite.



#### (4) CONDENSATION REACTIONS

The reaction in which two molecules of the same or different compounds combine to form a new compound with or without the elimination of a small molecule like  $H_2O$  or  $NH_3$  are called condensation reactions.

**Exercise Q3 (iv)** Define and explain aldol condensation along with mechanism.

##### (a) ALDOL CONDENSATION

Aldol condensation is a reaction in which two molecules of same or different carbonyl compound containing  $\alpha$ -hydrogen (hydrogen attached to the carbon atom next to carbonyl group) combine together to form aldol or ketol, which usually loses water molecule.

##### Mild Alkaline conditions:

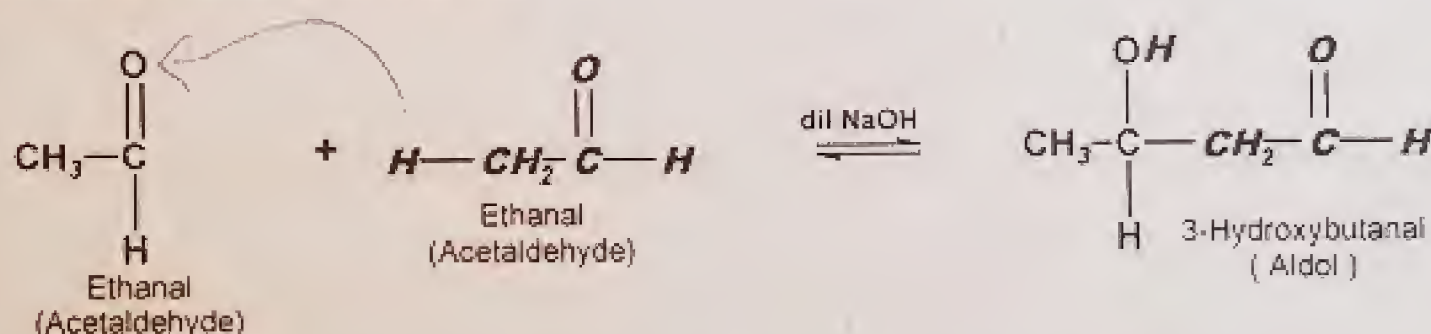
Aldol condensation takes place under mild alkaline conditions, for example in the presence of sodium carbonate, sodium bicarbonate, barium hydroxide, dilute sodium hydroxide or an alkoxide in low concentration.

##### Types:

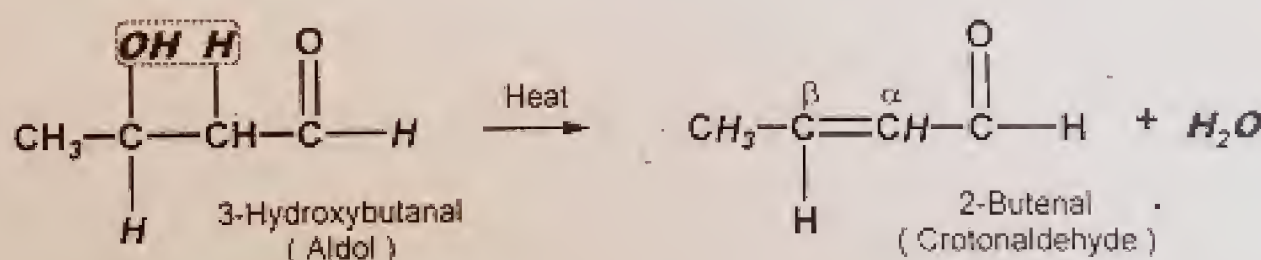
Aldol condensation can occur:

- (I) Between two aldehydes (identical or different)
- (II) Between an aldehyde and a ketone
- (III) Between two ketone (identical or different)

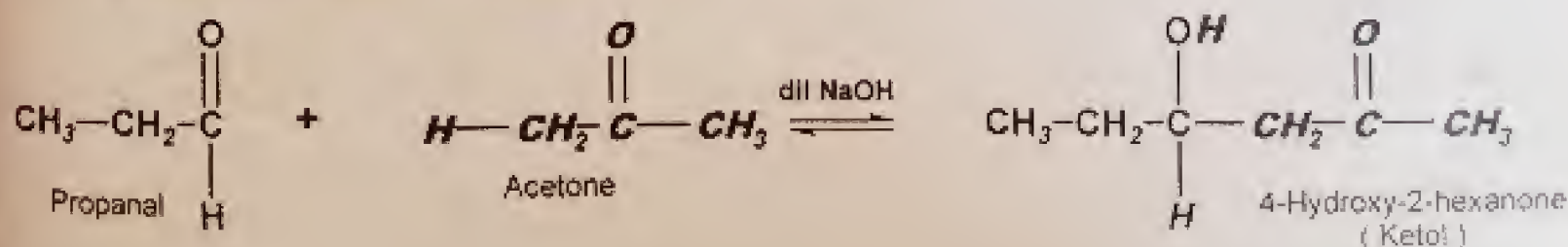
##### (i) Condensation between two aldehydes:



On heating aldol loses a molecule of water to form  $\alpha$ ,  $\beta$ -unsaturated aldehyde

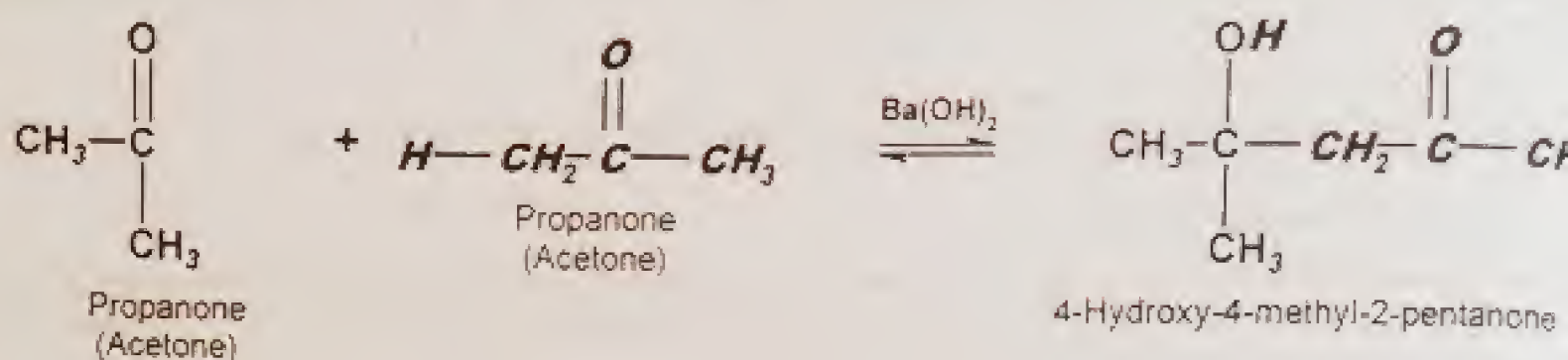


##### (ii) Condensation between aldehyde and ketone:





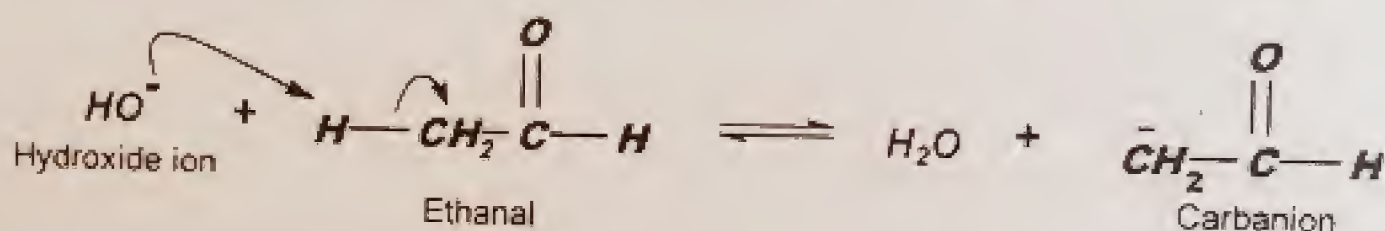
(III) Between two ketones



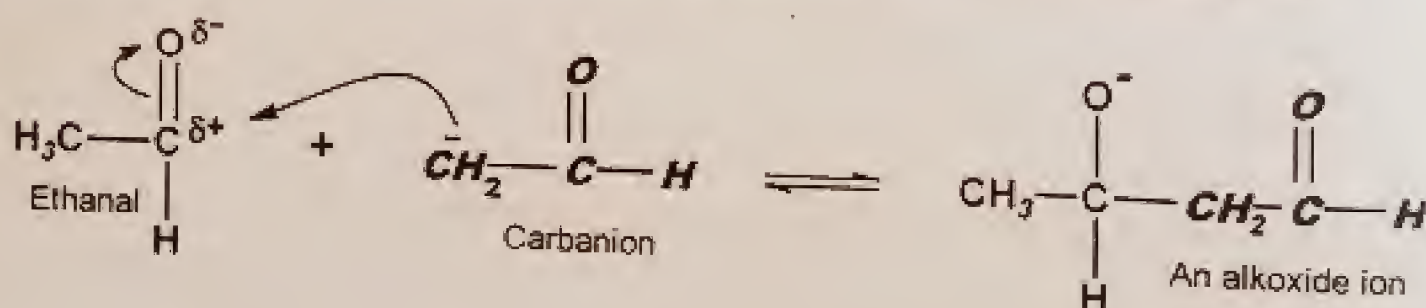
**Mechanism of Aldol Condensation:**

Following steps are involved in aldol condensation.

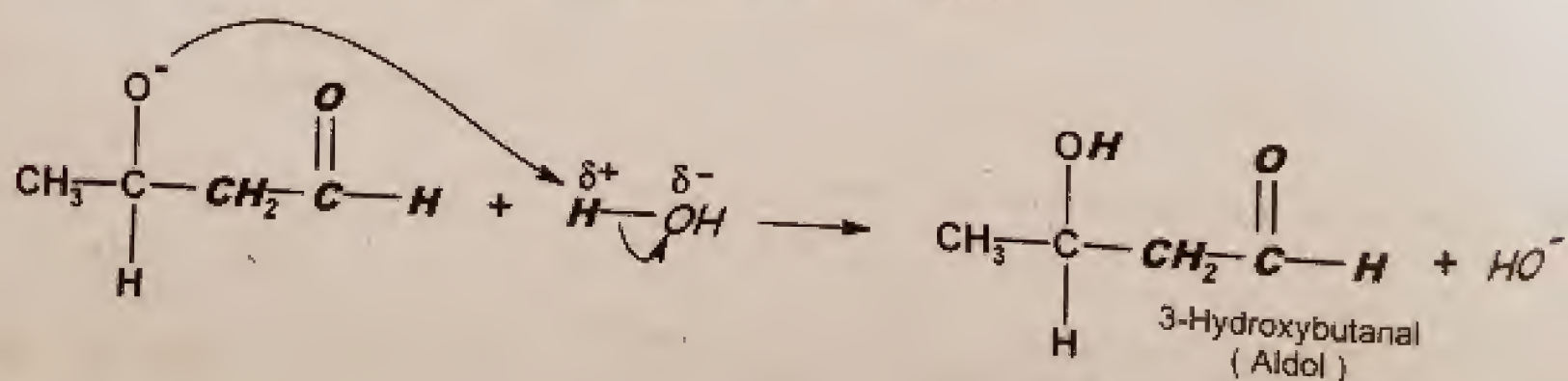
(1) Removal of a proton from  $\alpha$ -carbon of aldehyde/ketone by base: (Formation of nucleophile)



(2) Attack of nucleophile on carbonyl carbon to form alkoxide ion: (Formation of alkoxide ion)



(3) Removal of proton from water by alkoxide ion: (Formation of aldol)

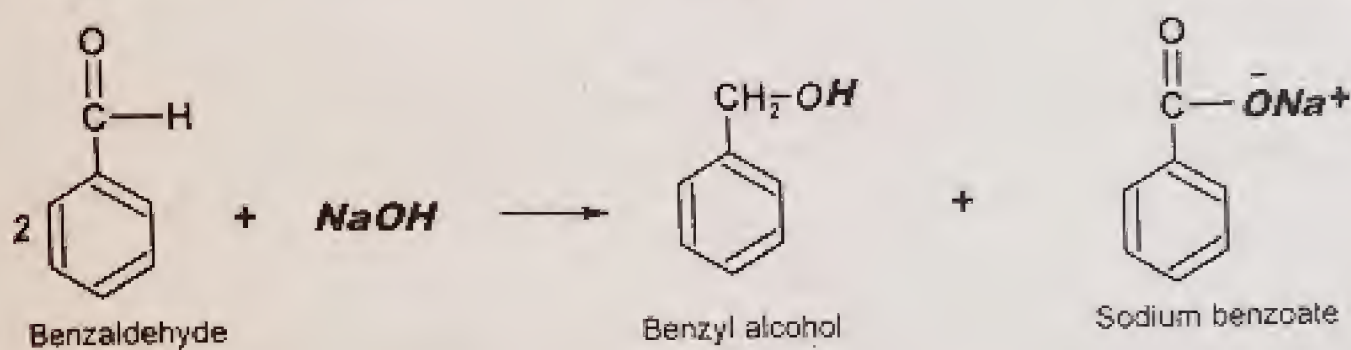
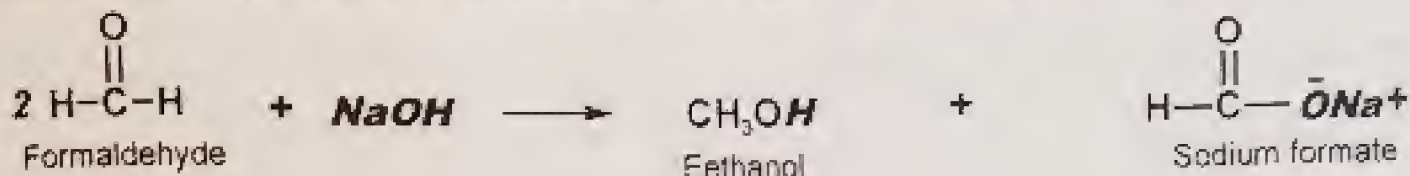




**Exercise Q3 (viii)** Which type of aldehydes give Cannizzaro's reaction? Explain with mechanism.

**(b) CANNIZZARO'S REACTION:**

- Aldehydes having no  $\alpha$ -hydrogen atoms undergo Cannizzaro's reaction.
- It is a disproportionate (self oxidation-reduction) reaction.
- Two molecules of the aldehyde are involved.
- One molecule is reduced into corresponding alcohol and the other is oxidized into the acid (in the salt form).
- The reaction carried out with 50% aqueous solution of sodium hydroxide at room temperature.

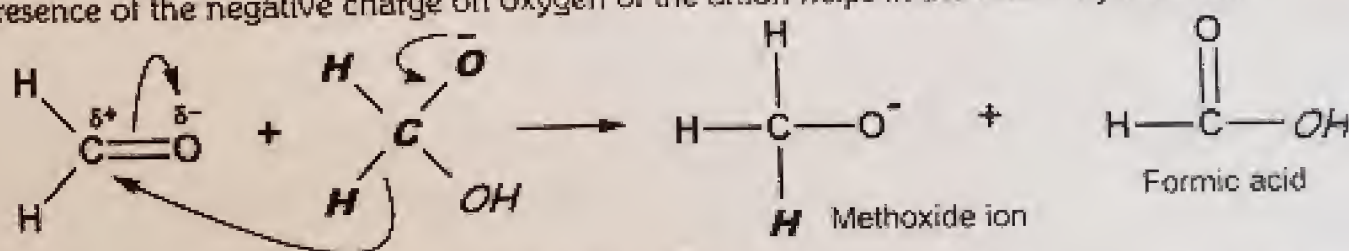


**Mechanism of Cannizzaro's Reaction:**

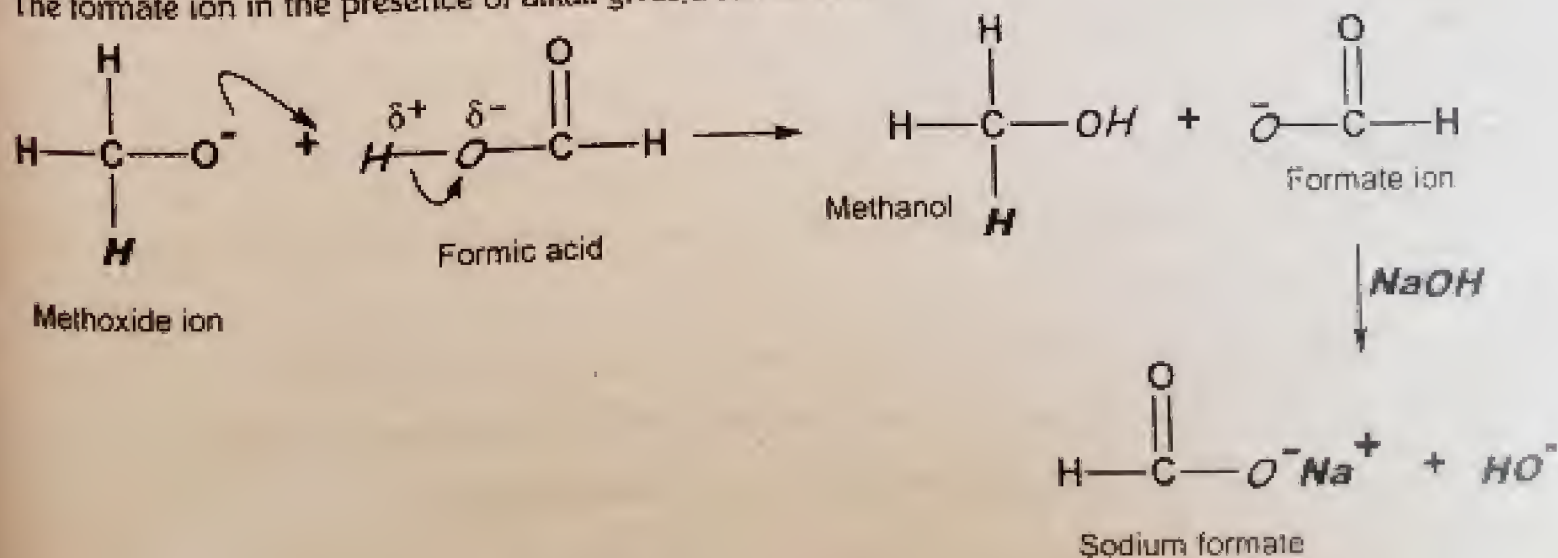
- The hydroxide ion acts as a nucleophile. It attaches on the electrophilic carbonyl carbon to form a complex anion.



- The anion transfers a hydride ion to second molecule of formaldehyde.
- The presence of the negative charge on oxygen of the anion helps in the loss of hydride ion.



- The methoxide ion acts as a base and abstracts a proton from formic acid to form methanol and formate ion.
- The formate ion in the presence of alkali gives a salt of acid.

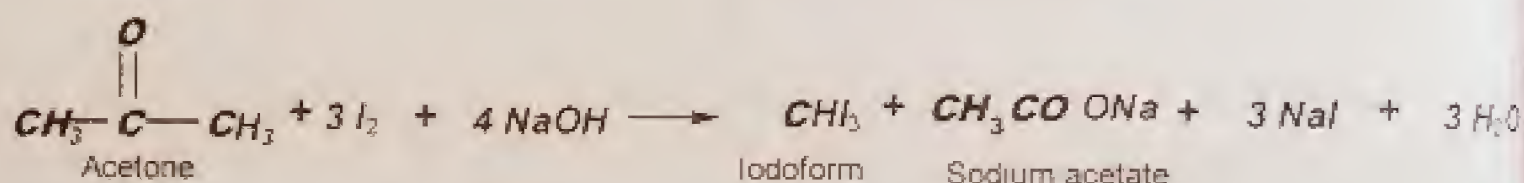
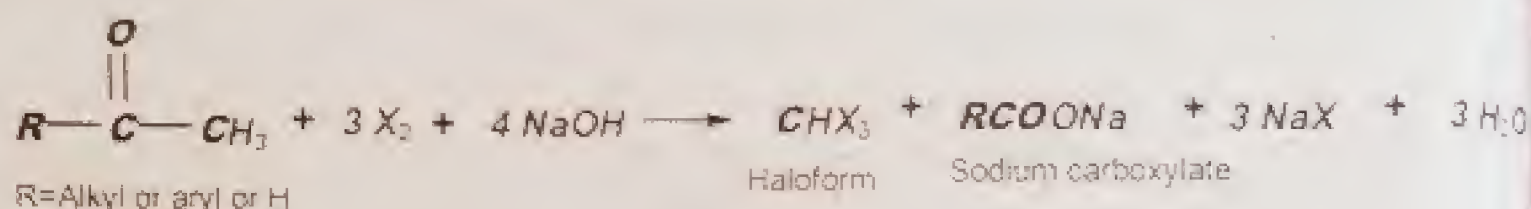




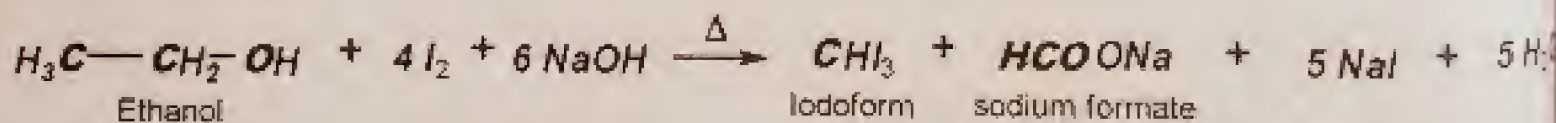
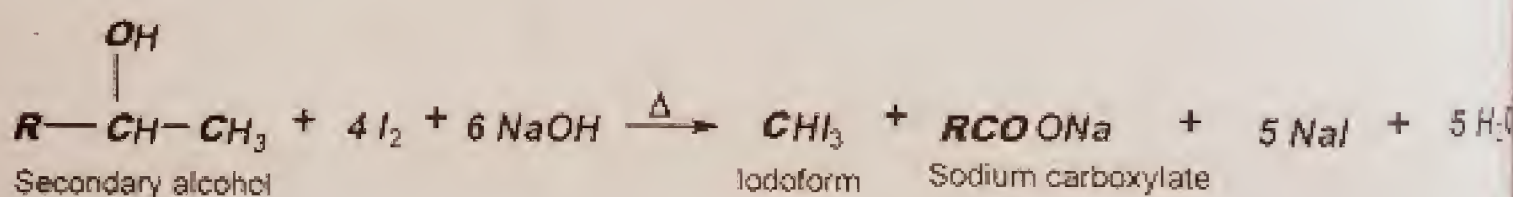
Exercise Q3 (v) Give detail of haloform reaction. Why it is called so?

### (5) HALOFORM REACTION

- Only acetaldehyde and methyl ketones react with halogens ( $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ) in the presence of sodium hydroxide to give haloform (chloroform, bromoform or iodoform) and sodium salt of the acid.



- Secondary alcohols containing the methyl group also undergo this reaction. Ethanol is the only primary alcohol that gives this reaction.



- Halogen reaction, is a convenient method for converting a methyl ketone to a carboxylic acid containing carbon atom less than parent compound.

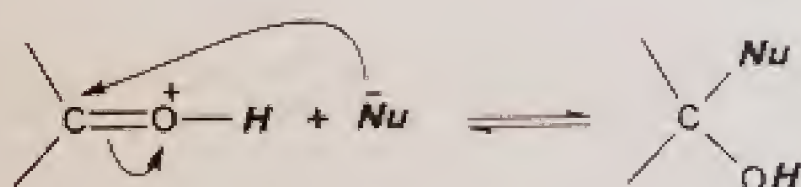
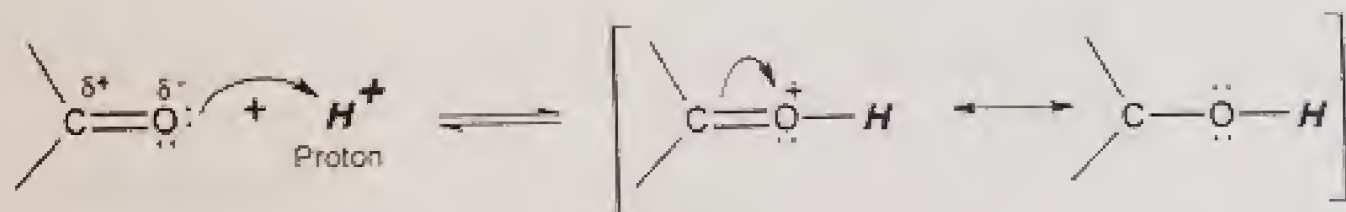
### iodoform test

- It is haloform reaction in which iodine and aqueous sodium hydroxide form water insoluble iodoform (a yellow solid).
- Iodoform test is used for distinguishing methyl ketones from other ketones.
- It is also used to distinguish ethanol from methanol and other primary alcohols.
- It can be used to distinguish acetaldehyde from other aldehydes.



## (ii) ACID CATALYSED NUCLEOPHILIC ADDITION REACTIONS

- The addition is initiated by the proton liberated by the acid, which combines with the carbonyl oxygen.
- It increases the electrophilic character of the carbonyl carbon and the attack of the weaker nucleophile on the electrophilic carbon becomes easy.

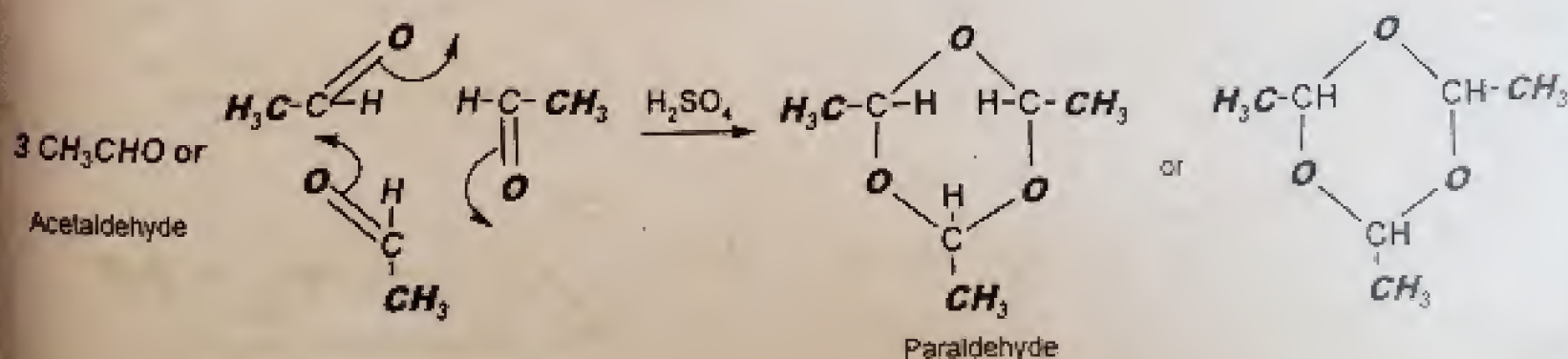
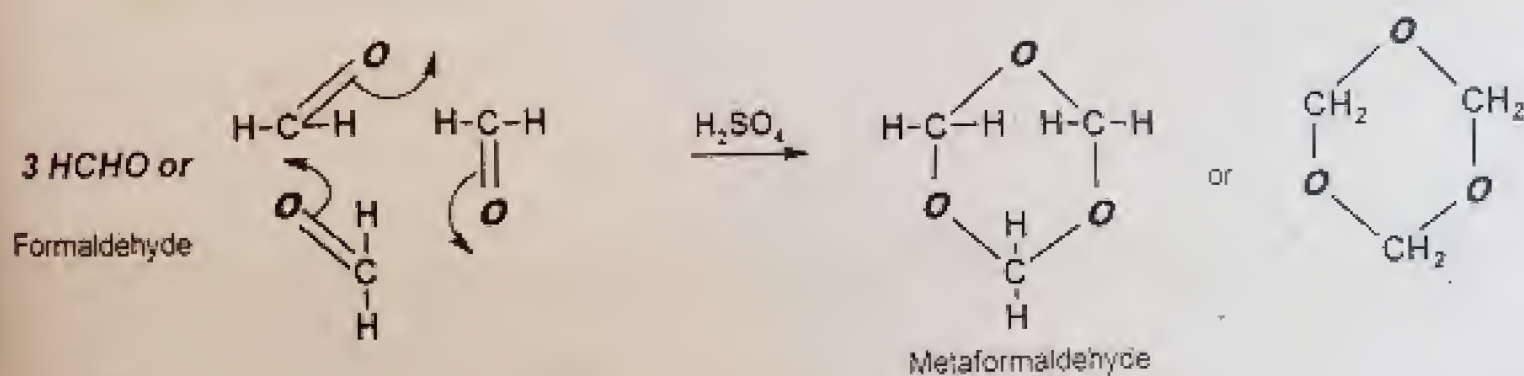


There are three types

- (1) Polymerization
- (2) Addition of ammonia derivatives
- (3) Addition of alcohols

### (1) POLYMERIZATION

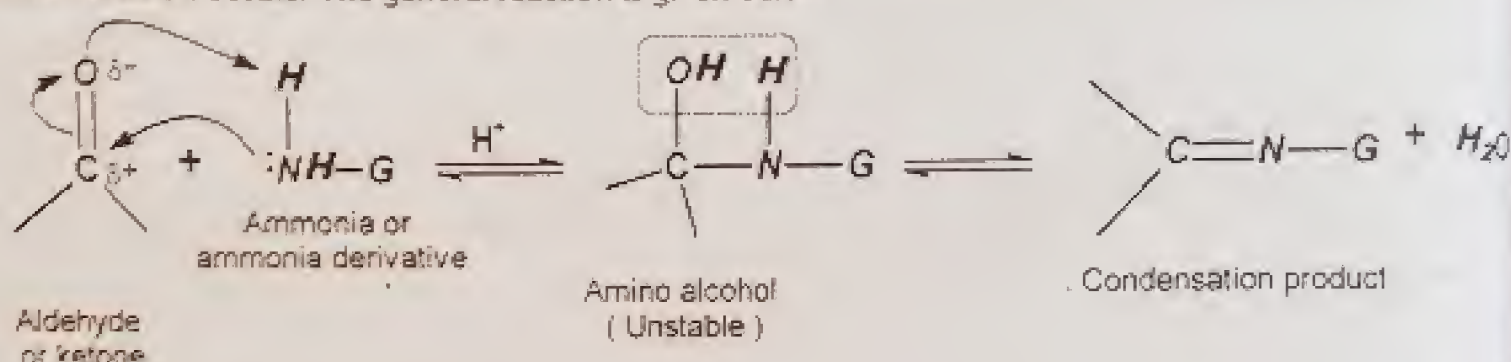
Both formaldehyde and acetaldehyde polymerize in the presence of dil.  $H_2SO_4$  to give metaformaldehyde and paraldehyde.





## (2) ADDITION OF AMMONIA DERIVATIVES

Aldehydes and ketones react with ammonia derivatives,  $G-NH_2$  to form compounds containing the group  $>C=N-G$ . The reaction is known as condensation reaction or addition-elimination reaction because water is lost after addition occurs. The general reaction is given below.

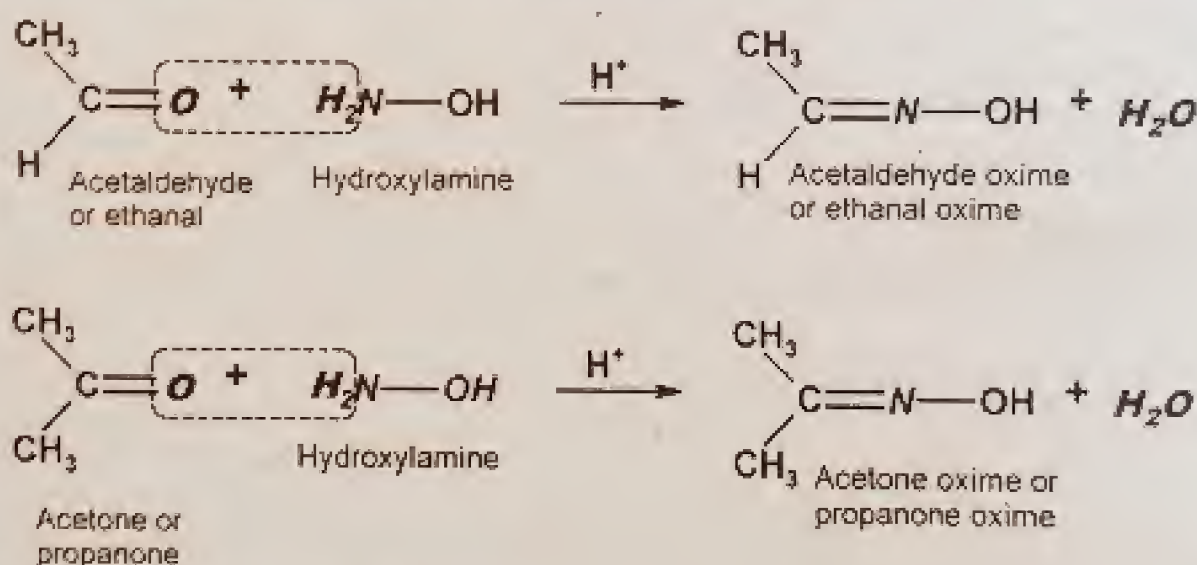


### Specific Examples:

Some commonly used ammonia derivatives are hydroxylamine,  $NH_2OH$ , hydrazine,  $NH_2NH_2$ , phenylhydrazine,  $C_6H_5NHNH_2$ , semicarbazide,  $NH_2NHCONH_2$ , and 2,4-dinitrophenylhydrazine,  $NH_2NHC_6H_3(NO_2)_2$ .

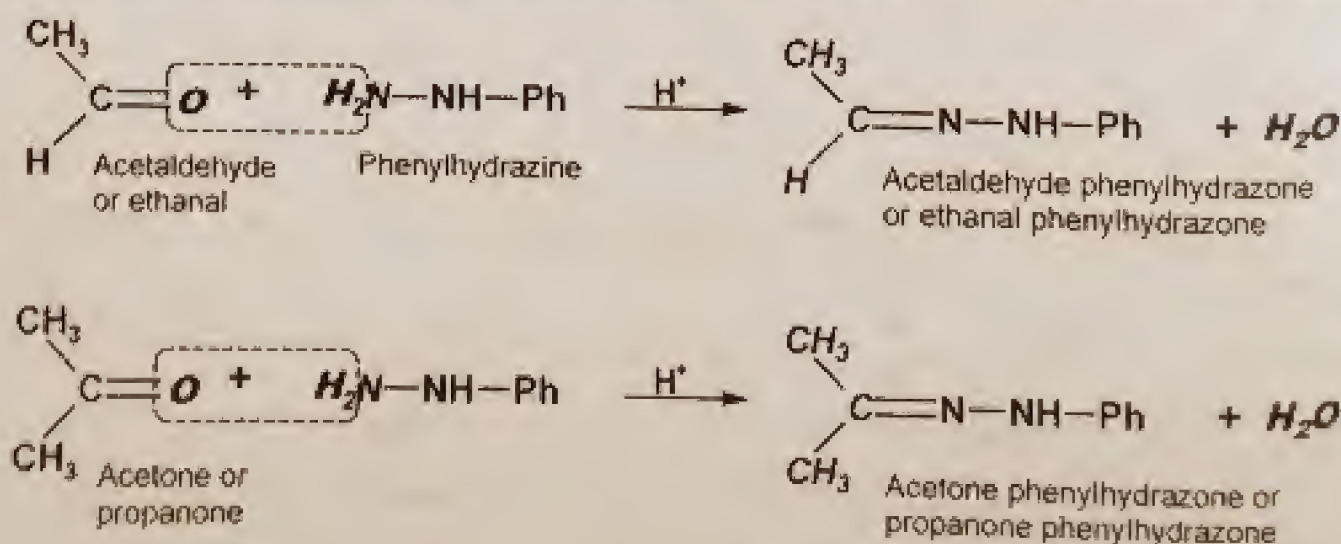
### REACTION WITH HYDROXYLAMINE

Aldehydes and ketones react with hydroxylamine to form oximes in the presence of an acid.



### REACTION WITH PHENYLHYDRAZINE

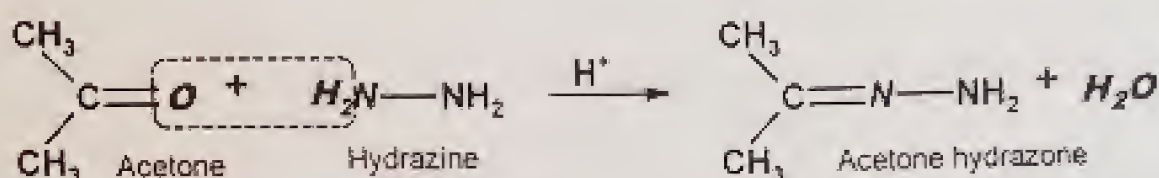
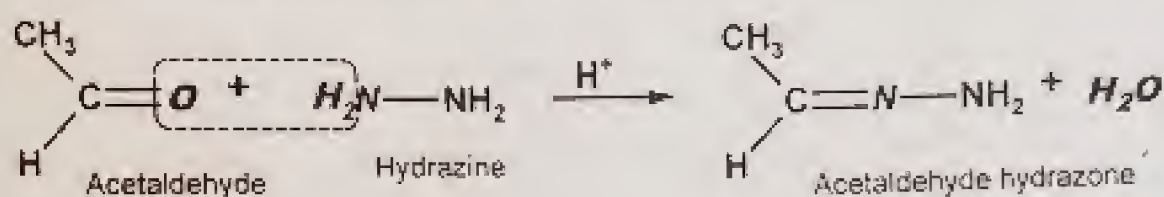
Aldehydes and ketones react with phenylhydrazine to form phenylhydrazones in the presence of an acid.





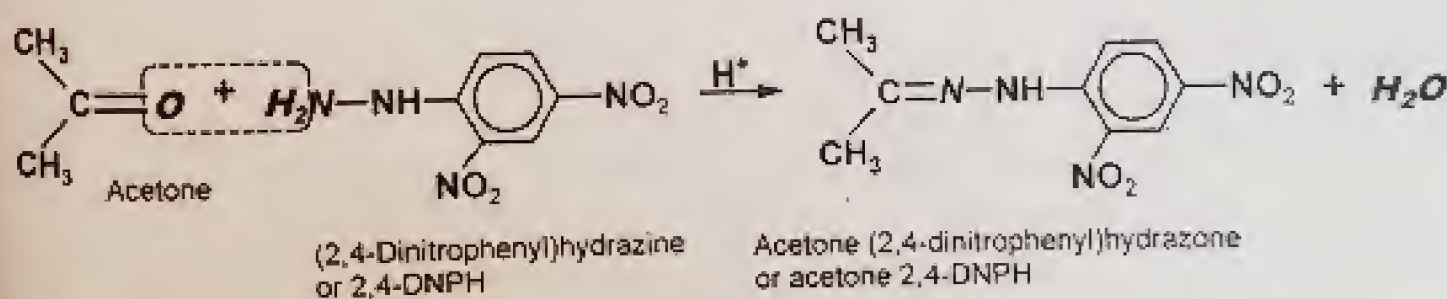
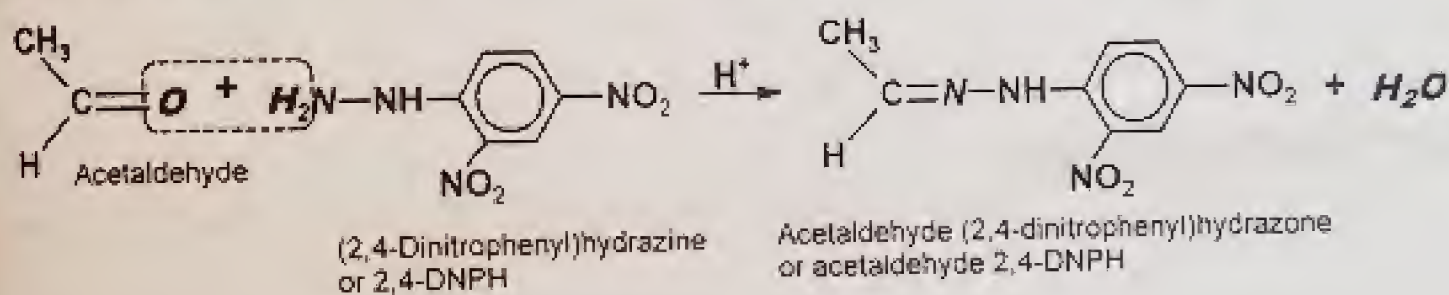
### REACTION WITH HYDRAZINE

Aldehydes and ketones react with hydrazine to form hydrazones in the presence of an acid.



### REACTION WITH 2,4-DINITROPHENYLHYDRAZINE

Aldehydes and ketones react with 2,4-dinitrophenylhydrazine to form 2,4-dinitrophenylhydrazone in the presence of an acid.

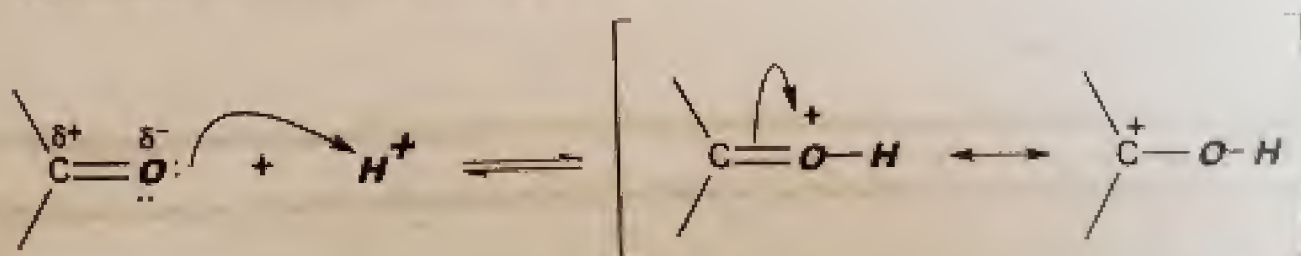


The reaction can be used for the identification of aldehydes and ketones because 2,4-dinitrophenylhydrazones are usually yellow or orange crystalline solids.

**Exercise Q3 (vii) What is the mechanism for addition of ammonia derivatives to carbonyl group?**

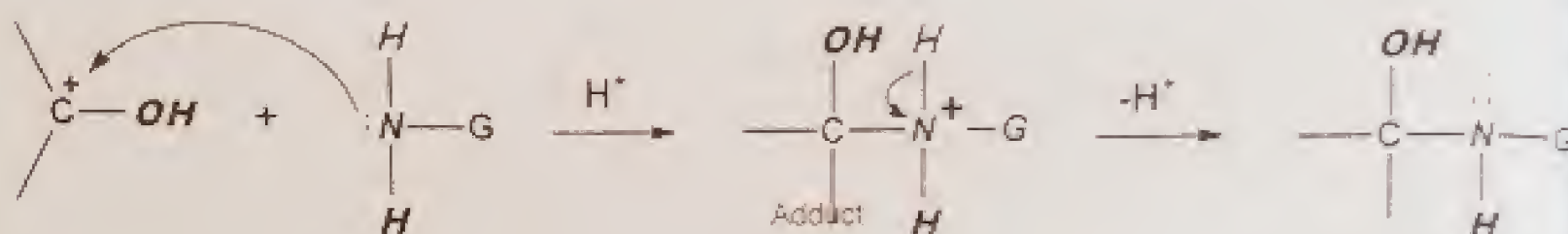
**Mechanism of the Reaction of ammonia derivatives**

**Step 1: Protonation of oxygen of the carbonyl group.**

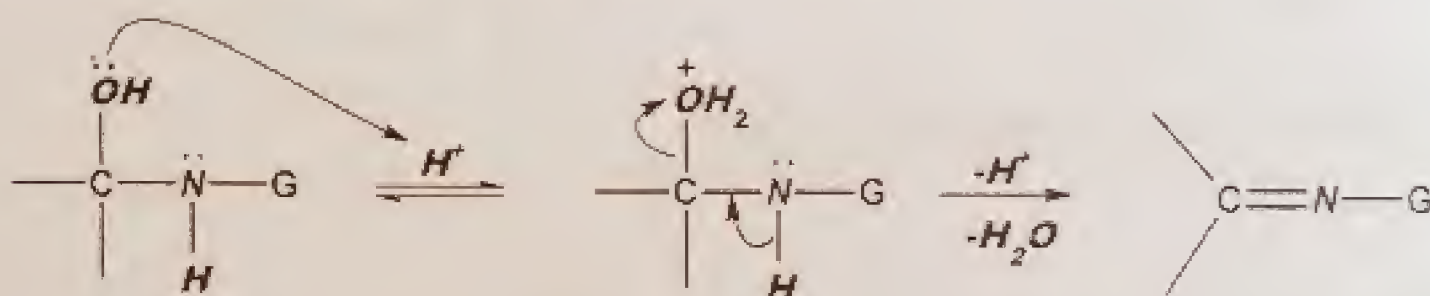




**Step 2:** Nucleophilic attack of nitrogen of ammonia derivative on the electrophilic positively charged carbon and deprotonation of the adduct.

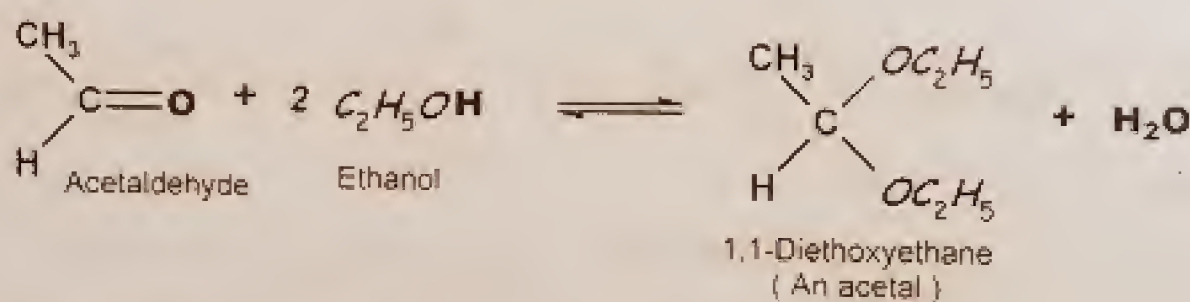


**Step 3:** Protonation of oxygen of hydroxyl group followed by the removal of water.



### (3) ADDITION OF ALCOHOLS

Aldehydes combine with alcohols in the presence of hydrogen chloride gas to form acetals. The hydrogen chloride acts as a catalyst.



The reaction may be used to protect the aldehyde group against alkaline oxidizing agents. To regenerate aldehyde, the acetal is hydrolysed in the presence of an acid.

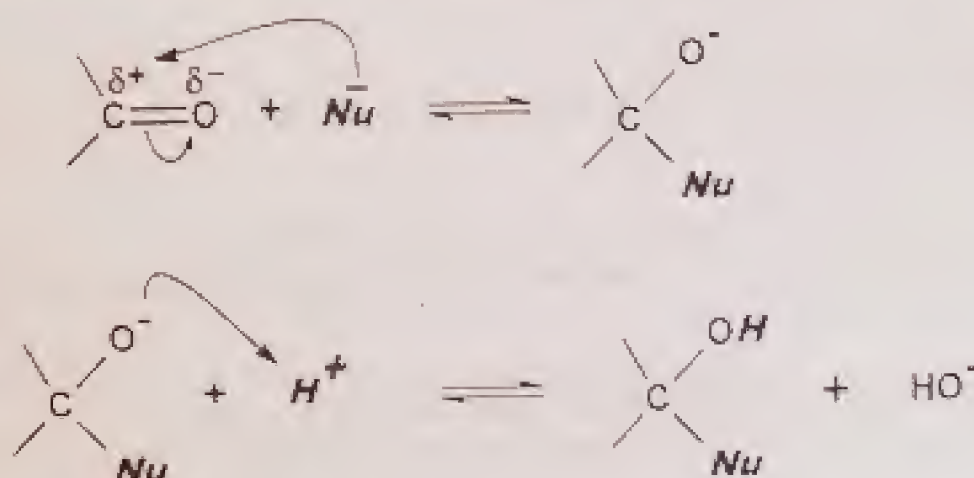


**Note:** Ketones do not react under these conditions.



## RELATIVE REACTIVITY OF ALDEHYDES AND KETONES

Overall a simple nucleophilic addition can be represented with curly arrows as follows:



The reactivity of aldehydes and ketones can be easily rationalized by considering the important resonance contributor which has charge separation with a +ve C and -ve O. In general the reactivity order towards nucleophiles is: **aldehydes > ketones** (see below)

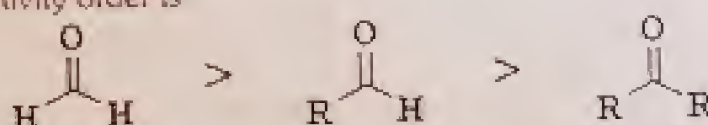
The substituents have two contributing factors on the reactivity at the carbonyl C.

(1) Size of the substituents attached to the C=O. Larger groups will tend to sterically hinder the approach of the nucleophile.

(2) The electronic effect of the substituent.

Alkyl groups are weakly electron donating so they make the C in the carbonyl less electrophilic and therefore less reactive towards nucleophiles.

Thus the reactivity order is



These trends are supported by the trends in the equilibrium data for the formation of hydrate.

	Carbonyl	K / M <sup>-1</sup>	% Hydrate	
Carbonyl	methanal	41	99.96	Hydrate
	ethanal	1.8 × 10 <sup>-2</sup>	50	
	2,2-dimethylpropanal	4.1 × 10 <sup>-3</sup>	19	
	propanone	2.5 × 10 <sup>-5</sup>	0.14	

$$(K = [\text{hydrate}]/[\text{C}=\text{O}])$$

Thus, methanal has high value of K, so its equilibrium appreciably goes to the right. Hence, it is most reactive

## REDUCTION OF ALDEHYDES AND KETONES

### REDUCTION TO HYDROCARBONS





### Clemmensen Reduction (acidic conditions)

- $\text{Zn(Hg)}$  in  $\text{HCl}$  reduced the  $\text{C=O}$  into  $-\text{CH}_2-$

### Wolff-Kishner Reduction (basic conditions)

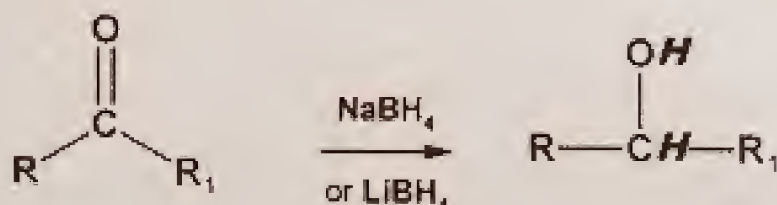
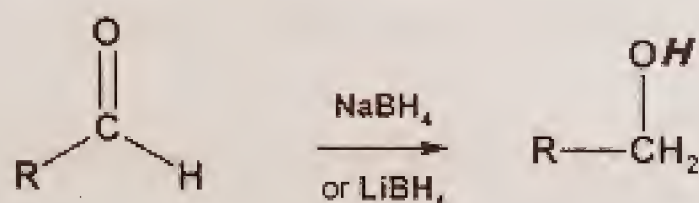
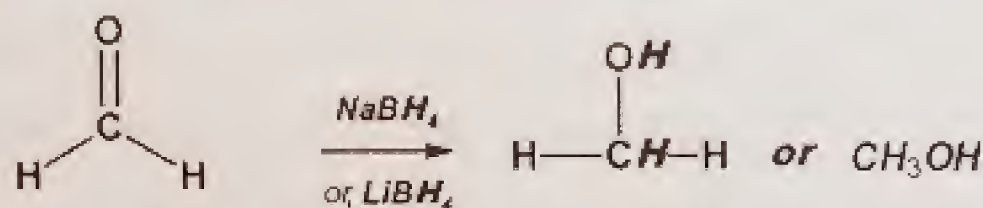
- $\text{NH}_2\text{NH}_2$  /  $\text{KOH}$  / ethylene glycol (a high boiling solvent) reduces the  $\text{C=O}$  into  $-\text{CH}_2-$

### Overview

- These reduction methods do not reduce  $\text{C=C}$ ,  $\text{C}\equiv\text{C}$  or  $-\text{CO}_2\text{H}$
- The choice of method should be made based on the tolerance of other functional groups to the acidic or basic reaction conditions.

## HYDRIDE REDUCTIONS OF ALDEHYDES AND KETONES

Hydride reacts with the carbonyl group,  $\text{C=O}$ , in aldehydes or ketones to give alcohols.



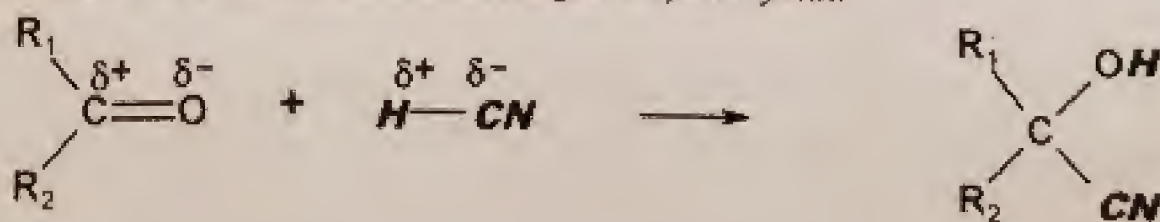
- Aldehydes and ketones are most readily reduced with hydride reagents.
- The reducing agents  $\text{LiAlH}_4$  and  $\text{NaBH}_4$  act as a source of  $4\text{H}^-$  (hydride ion).
- Overall 2 H atoms are added across the  $\text{C=O}$  to give  $\text{H-C-O-H}$ .
- The substituents on the carbonyl tell the nature of the product alcohol.
- Reduction of methanal (formaldehyde) gives methanol.
- Reduction of other aldehydes gives **primary** alcohols.
- Reduction of ketones gives **secondary** alcohols.
- The acidic work-up converts an intermediate metal alkoxide salt into the desired alcohol via a simple acid-base reaction.

## CLASSIFICATION SUMMARY OF REACTIONS OF CARBONYL COMPOUNDS WITH DIFFERENT NUCLEOPHILES

### (1) USING CARBON NUCLEOPHILES

#### CYANOHYDRIN FORMATION

- Cyanide adds to aldehydes and ketones to give a cyanohydrin.

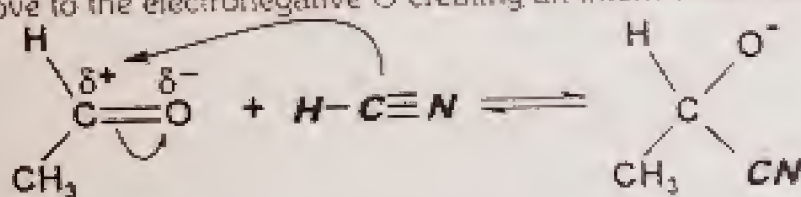




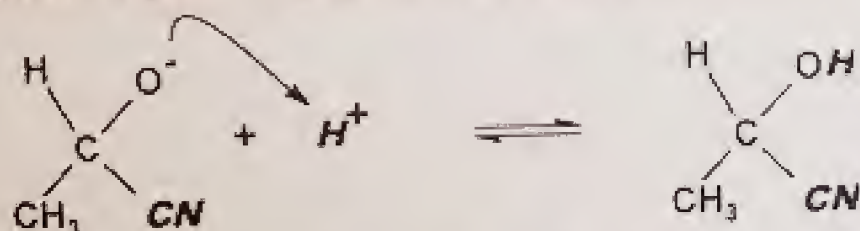
- The reaction is usually carried out using NaCN or KCN with HCl.
- HCN is a fairly weak acid, but **very toxic**.
- The reaction is useful since the cyano group can be converted into other useful functional groups ( $-\text{CO}_2\text{H}$  or  $-\text{CH}_2\text{NH}_2$ )

### NUCLEOPHILIC ADDITION OF CYANIDE TO AN ALDEHYDE

**Step 1:**  
The nucleophilic C in the cyanide adds to the electrophilic C in the polar carbonyl group, electrons from the  $\text{C}=\text{O}$  move to the electronegative O creating an intermediate alkoxide.



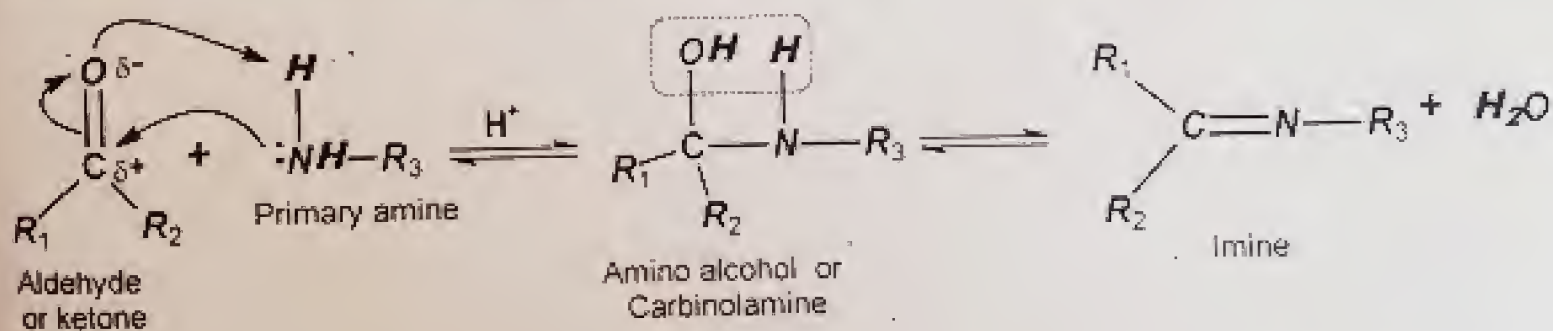
**Step 2:**  
An acid/base reaction. Protonation of the alkoxide oxygen creates the cyanohydrin product.



### (2) USING NITROGEN NUCLEOPHILES

#### Reactions of Primary Amine derivatives

Primary amines,  $\text{R-NH}_2$  or  $\text{ArNH}_2$ , undergo nucleophilic addition with aldehydes or ketones to give **carbinolamines** which then dehydrate to give substituted **imines**.



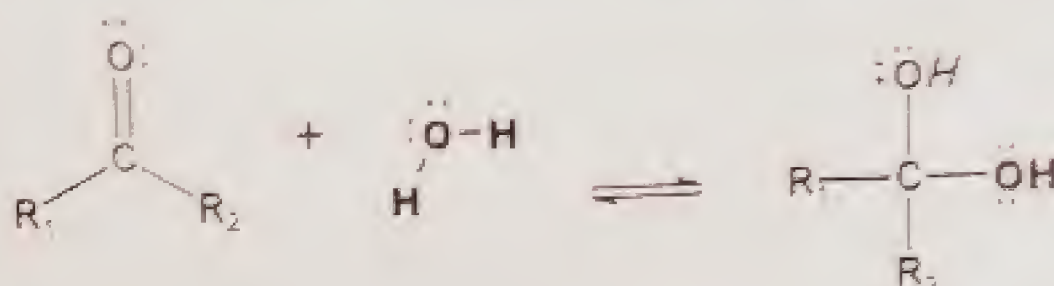
- The reactions are usually carried out in an acidic buffer to activate the  $\text{C}=\text{O}$  and facilitate dehydration but without inhibiting the nucleophile.
- Systems of the general type  $\text{H}_2\text{N-G}$  undergo this type of reaction and can be used



### (3) USING OXYGEN NUCLEOPHILES

#### Formation of Hydrates

Aldehydes and ketones react with water to give 1,1-geminal diols known as hydrates.



- In general, hydrates are not stable enough to be isolated as the equilibrium shifts back to starting materials.
- However, hydrates are the reactive species in the oxidation of aldehydes to acids.
- Understanding the mechanism is useful before looking at the very closely related reactions of alcohols.

#### MECHANISM FOR THE ACID catalyzed FORMATION OF HYDRATES

##### Step 1:

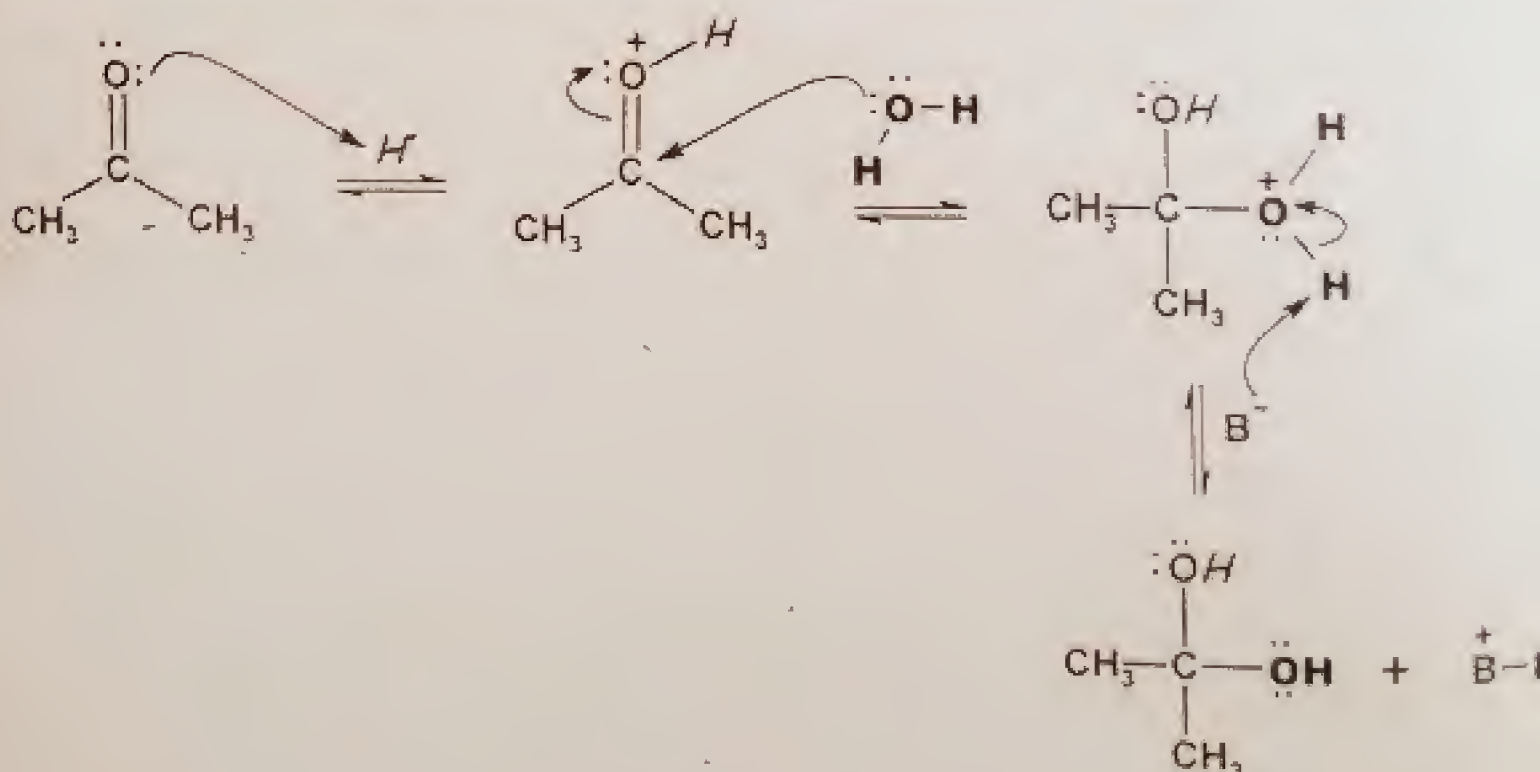
An acid/base reaction. Since there is only a weak nucleophile we need to activate the carbonyl by protonating on O.

##### Step 2:

The nucleophilic O in the water attacks the electrophilic C in the C=O, breaking the  $\pi$ -bond and giving electrons to the positive O.

##### Step 3:

An acid/base reaction. Deprotonation of the oxonium ion neutralizes the charge giving the hydrate.

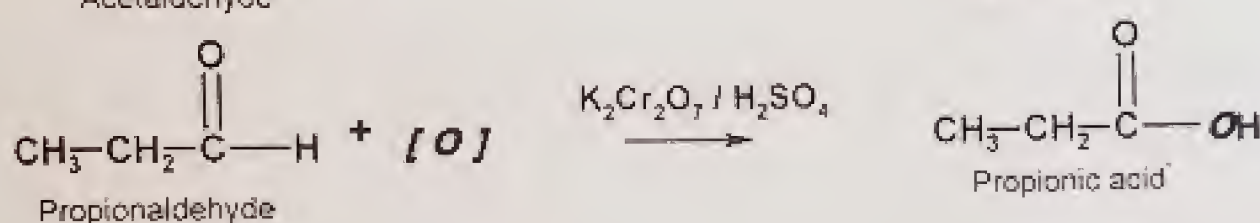
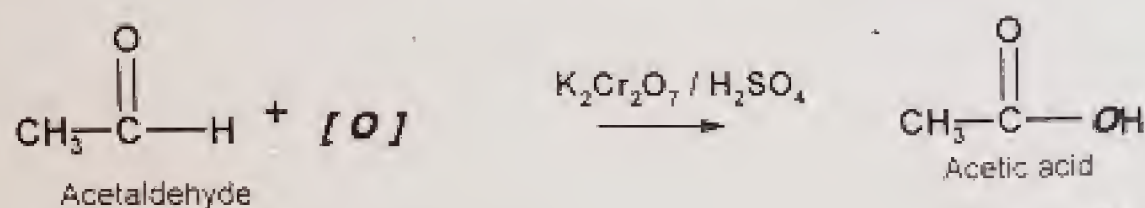




## OXIDATION REACTIONS

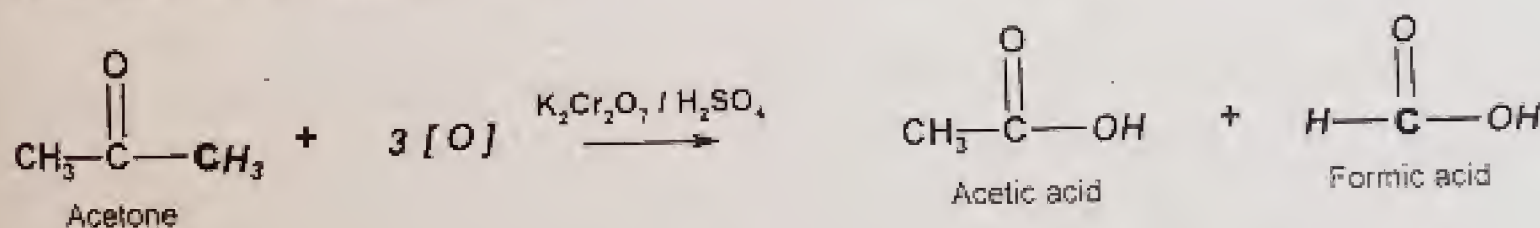
### OXIDATION OF ALDEHYDES

- Mild oxidizing agents like Tollen's reagent, Fehling's solution and Benedict's solution easily oxidize aldehydes to carboxylic acids.
- They are also oxidized by strong oxidizing agents such as  $K_2Cr_2O_7/H_2SO_4$ ,  $KMnO_4/H_2SO_4$ , and dilute nitric acid.
- The hydrogen atom attached to the carbonyl group in aldehydes is oxidized to OH group in these reactions.

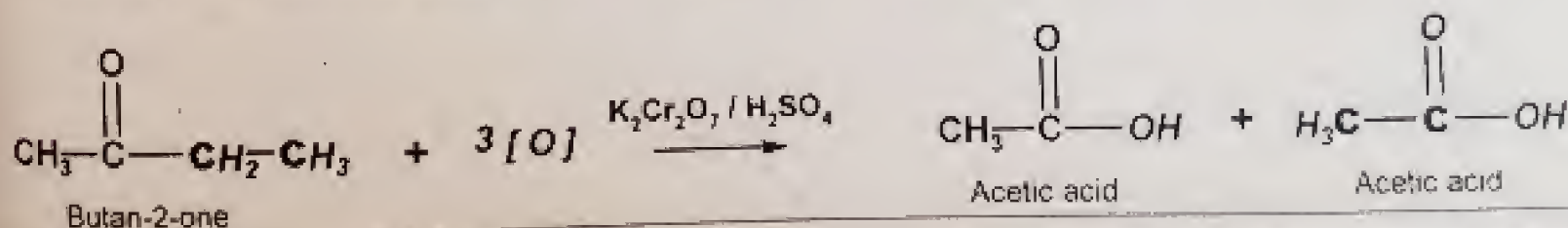


### OXIDATION OF KETONES

- Ketones are only oxidized by strong oxidizing agents such as  $K_2Cr_2O_7/H_2SO_4$ ,  $KMnO_4/H_2SO_4$  and conc.  $HNO_3$ .
- The carbon atom joined to the smaller number of hydrogen atoms is oxidized.
- In case of symmetrical ketones only one carbon atom adjacent to the carbonyl group is oxidized and mixture of two carboxylic acids is always obtained.

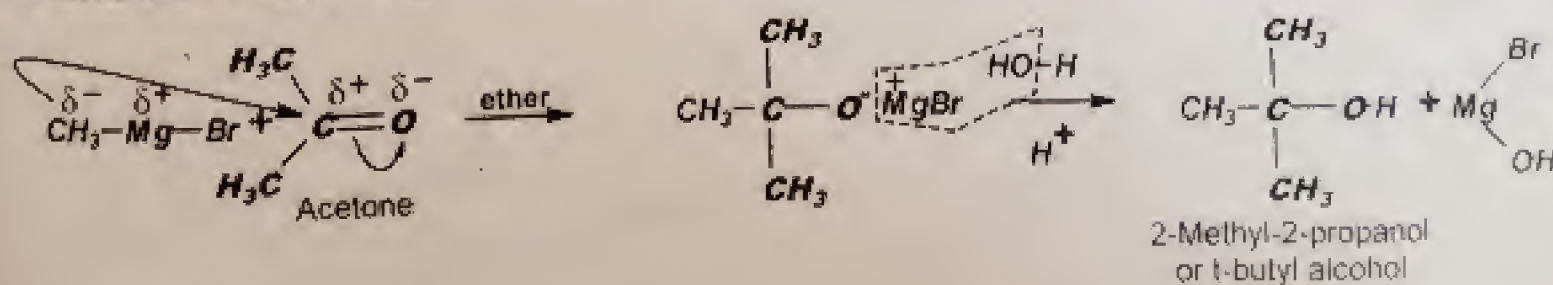


- However, in case of unsymmetrical ketones, the carbon atom joined to the smaller number of hydrogen atoms is preferentially oxidized and the carbonyl group remains with the smaller alkyl group.



## SOME IMPORTANT CONVERSIONS

### (i) Acetone into t-butyl alcohol





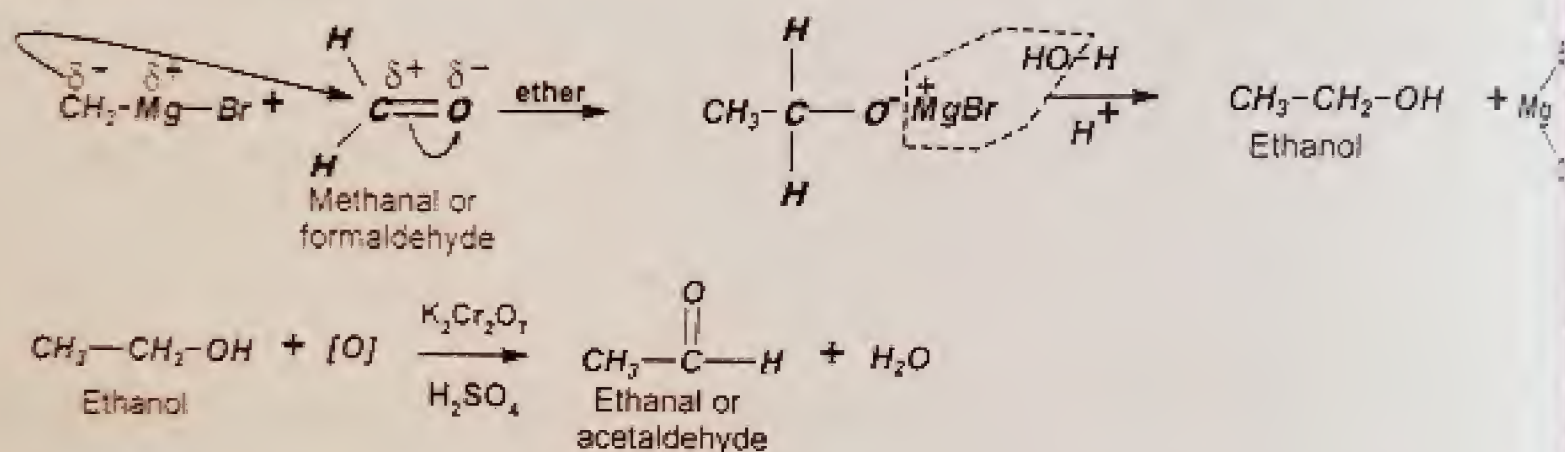
(iii) Propanal into 1-propanol



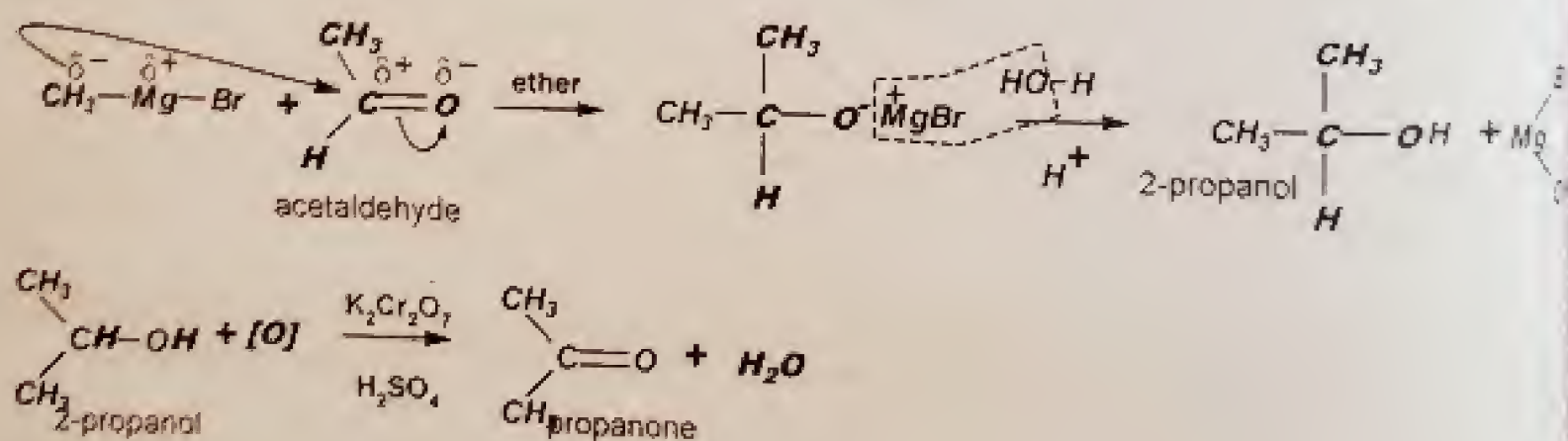
(iii) Propanone into 2-propanol



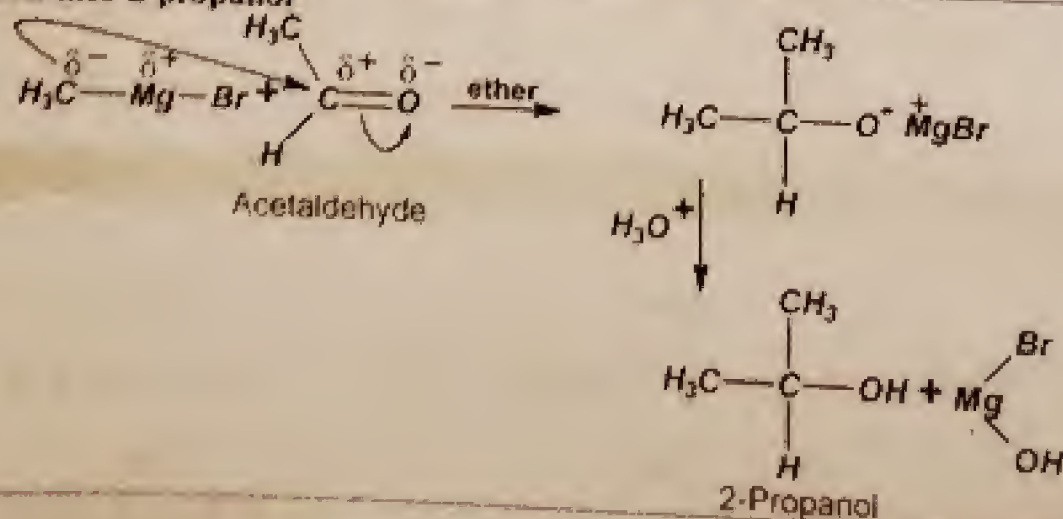
(iv) Methanal into ethanal



(v) Ethanal into propanone

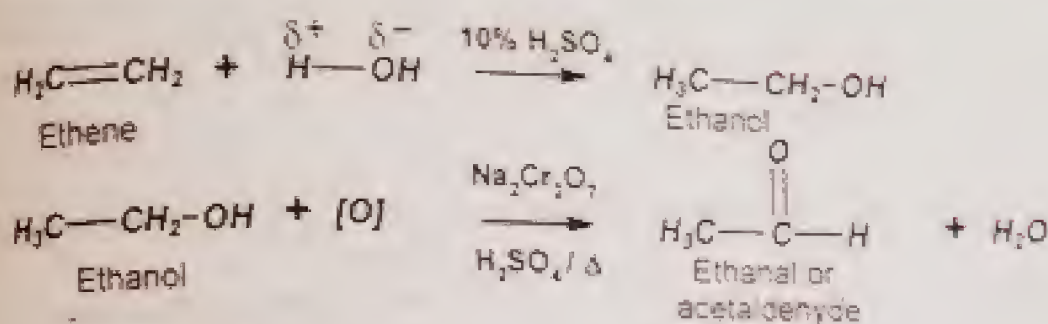


(vi) Ethanal into 2-propanol

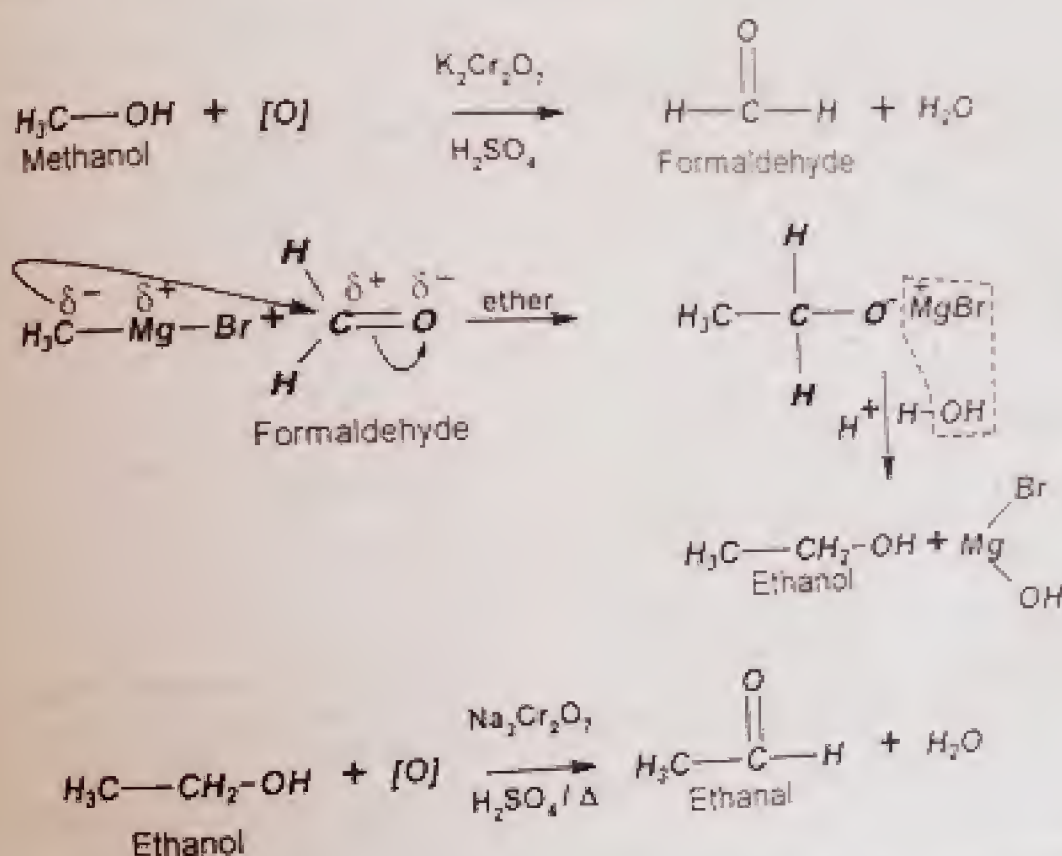




Ethene into ethanal



Methanol into ethanal



## SOCIETY, TECHNOLOGY AND SCIENCE

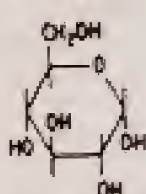
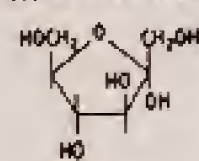
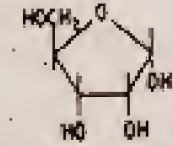



### Sugars Glucose and Fructose - Naturally occurring carbonyl compounds

- Sugars are sweet tasting soluble carbohydrates.
- Carbohydrates derive their name for the fact that they are composed of carbon, hydrogen and oxygen with H and O in the ratio of 2:1 as in water.
- Monosaccharides such as glucose are usually pentoses or hexoses, i.e. they contain 5 or 6 carbon atoms in their molecules.
- Disaccharides such as sucrose consist of two monosaccharide molecules joined by the elimination of a molecule of water.
- Polysaccharides such as starch are made up of many Monosaccharides units joined together. The Monosaccharides all have asymmetric molecules. They therefore exhibit optical isomerism.
- The most obvious feature of the structure of the Monosaccharides and disaccharides is the presence of large number of -OH groups. These give them a large capacity for hydrogen bonding, so they are in volatile solids, soluble in water. The presence of -OH groups on several adjacent carbon atoms in the molecule is thought to be responsible for the sweet taste of sugars.
- The most obvious feature of the structure of the Monosaccharides and disaccharides is the presence of large number of -OH groups. These give them a large capacity for hydrogen bonding, so they are involatile solids, soluble in water.



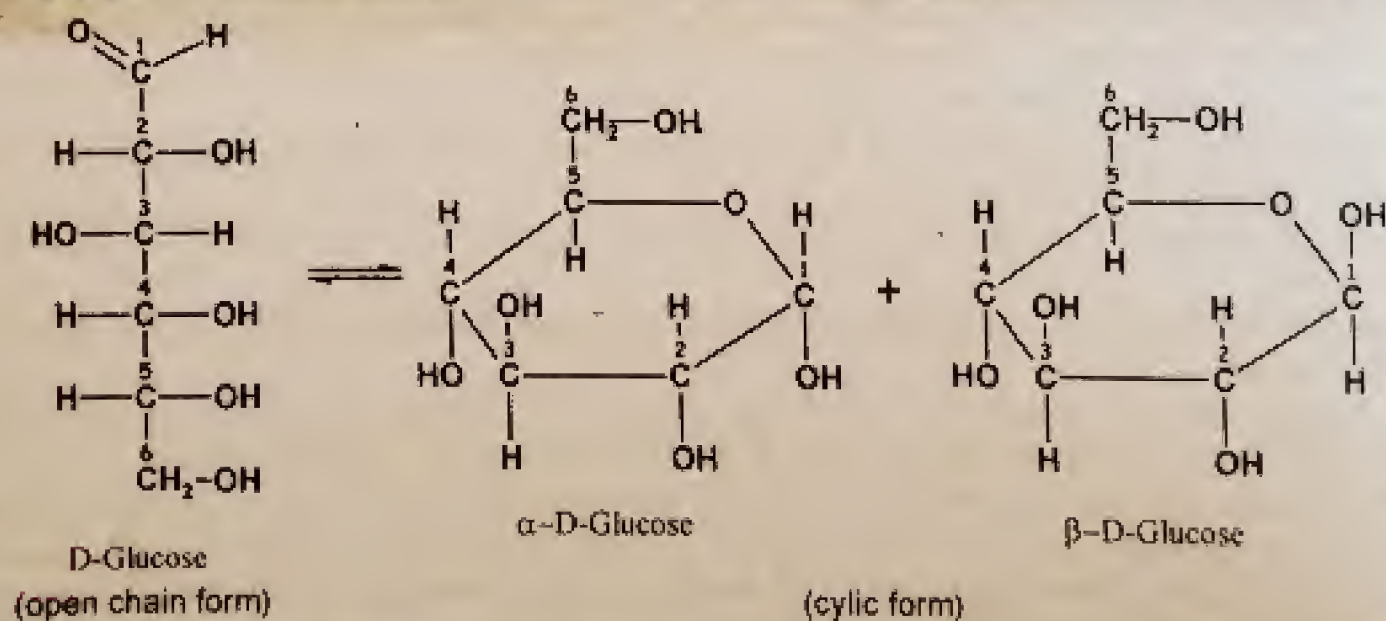
- The presence of  $-OH$  groups on several adjacent carbon atoms in the molecule is thought to be responsible for the sweet taste of sugars.
- Sugars also show many properties in solution that are typical of carbonyl compounds. For example, glucose gives a crystalline condensation compound with 2,4-dinitrophenylhydrazine. This is surprising since the structure of glucose contains no carbonyl group.

Some common carbohydrates. In the ring structures, the C atoms in the ring and the H atoms attached to them have been omitted, for clarity

Name	Type	Structure	Occurrence
glucose	monosaccharide, aldose, hexose		occurs abundantly in plants and animals
fructose	monosaccharide, ketose, hexose		in fruit and honey
ribose	monosaccharide, aldose, pentose		component of the molecules of ribonucleic acid (RNA) and vitamin B12
sucrose	disaccharide		sugar cane, sugar beet (commonly simply called 'sugar')
maltose	disaccharide		malt
lactose	disaccharide		milk
starch	polysaccharide	chains of glucose units	plant storage organs, e.g. potato, wheat grain
cellulose	polysaccharide	chains of glucose units (linked differently to those in starch)	structural material of plants

The carbonyl properties possessed by glucose arise from the fact that in addition to its normal ring form it can exist as an open chain form.

### Glucose - An example of aldehyde

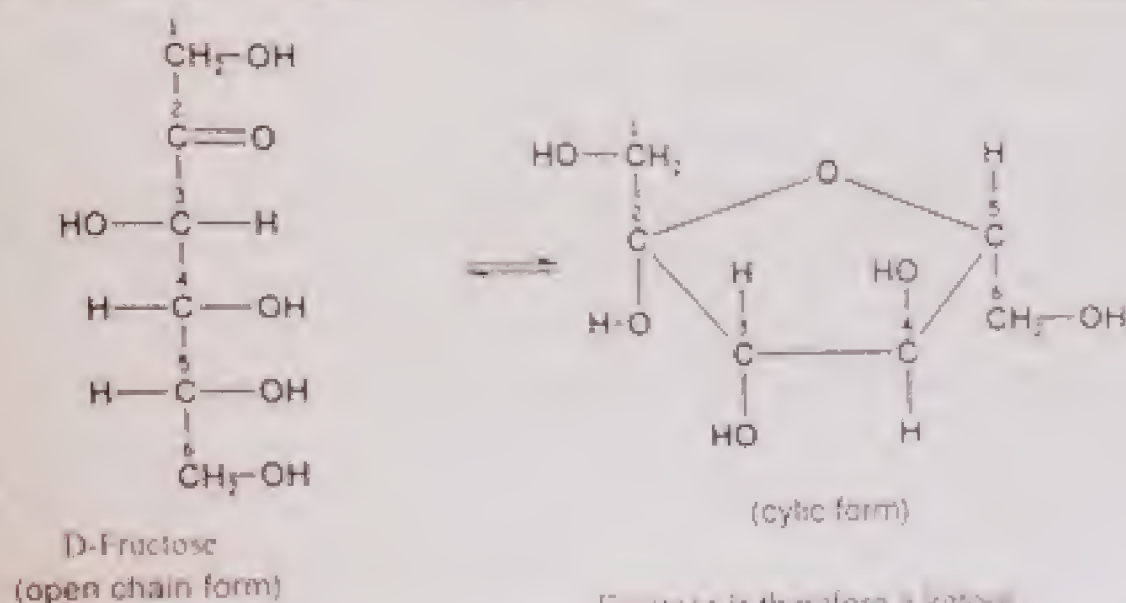


- The two forms are readily inter-converted and in aqueous solution about 1% of glucose molecules exist in the open chain form.



- This form carries an aldehyde group, so glucose has several properties typical of an aldehyde. It is sometimes called an aldose.
- Thus, in addition to the condensation reaction already mentioned glucose shows the reducing properties typical of an aldehyde.
- The reduction of Fehling's solution (or Benedict's solution) is a standard test for glucose and other reducing sugars.

### Fructose - An example of Ketone



### Why does the open chain form of glucose and other sugars change to the ring form?

It is a result of the tendency of the carbonyl group to undergo nucleophilic addition. The nucleophile involved is the oxygen atom of one of the -OH group of the same molecule. An internal nucleophilic addition reaction occurs, forming a ring.

### DO YOU KNOW?

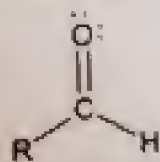
- 40% aqueous solution of formaldehyde is known as formalin, which is used in the preservation of biological specimens.
- Acetone is widely used as solvents in industry, the laboratory and the home.
- Formaldehyde is used as depolourising agent in vat dyeing.
- Formaldehyde is used in silvering of mirrors.

### QUICK QUIZ-2

(I) What is functional group of carbonyl compounds? Write their general formula?

Carbonyl compounds are aldehydes and ketones. Their functional group is carbonyl group ( $>\text{C}=\text{O}$ ). The compound in which carbonyl group is directly bonded to at least one hydrogen atom are called aldehydes.

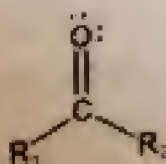
Their general formula is



where R = H or alkyl group

The compounds in which carbonyl group is directly bonded to two carbon atoms are called ketones. In these compounds C = O group occurs within chain.

Their general formula is



where R<sub>1</sub> and R<sub>2</sub> are alkyl or aryl groups



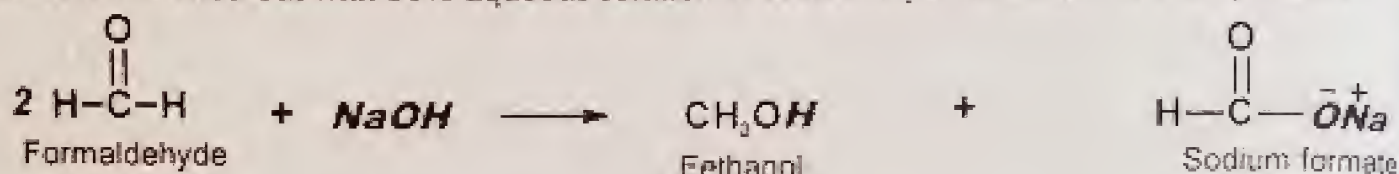
**(2) What types of aldehydes used in Cannizzaro's reactions**

Aldehydes having no  $\alpha$ -hydrogen atoms undergo Cannizzaro's reaction.

e.g. Formaldehyde,  $\text{HCHO}$ ; Benzaldehyde,  $\text{C}_6\text{H}_5\text{CHO}$  etc.

**(3) What is Cannizzaro's reaction?**

- Aldehydes having no  $\alpha$ -hydrogen atoms undergo Cannizzaro's reaction.
- It is a disproportionate (self oxidation-reduction) reaction.
- Two molecules of the aldehyde are involved. One molecule is reduced into corresponding alcohol, the other is oxidized into the acid (in the salt form).
- The reaction carried out with 50% aqueous solution of sodium hydroxide at room temperature.



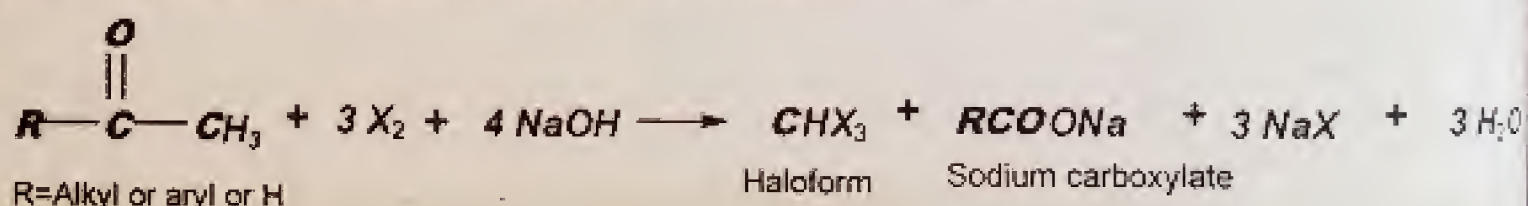
**(4) Which types of carbonyl compound condense to form an aldol?**

Aldehydes having at least one  $\alpha$ -hydrogen atoms undergo Aldol Condensation reaction.

e.g. Acetaldehyde,  $\text{CH}_3\text{CHO}$  etc.

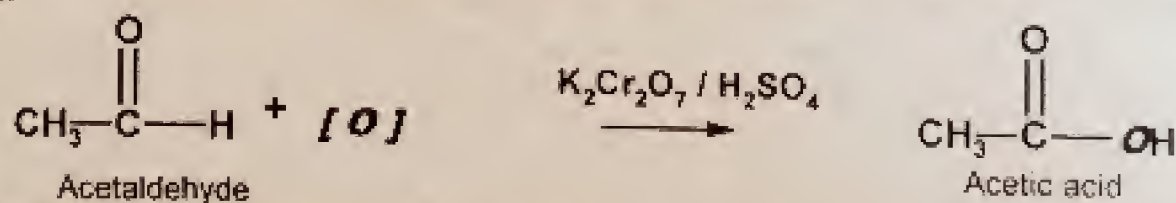
**(5) What is haloform reaction?**

Acetaldehyde, ethanol, methyl ketones and secondary alcohols with methyl group at  $\alpha$ -carbon, react with halogens ( $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ) in the presence of sodium hydroxide to give haloform (chloroform, bromoform, iodoform) and sodium salt of the acid. This reaction is called haloform reaction.



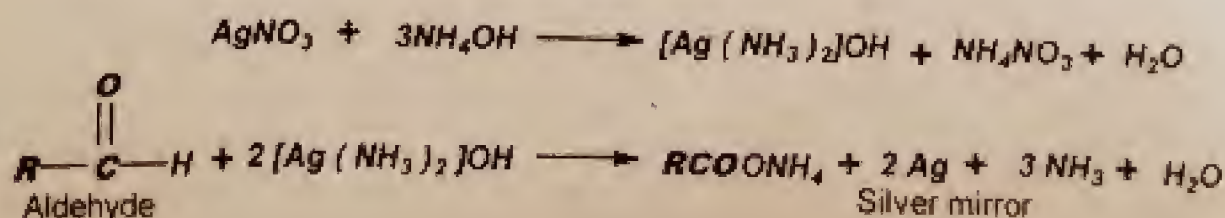
**(6) Give the oxidation of reactions of aldehydes**

- Mild oxidizing agents like Tollen's reagent, Fehling's solution and Benedict's solution easily oxidize aldehydes to carboxylic acids.
- They are also oxidized by strong oxidizing agents such as  $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ ,  $\text{KMnO}_4/\text{H}_2\text{SO}_4$  and nitric acid.
- The hydrogen atom attached to the carbonyl group in aldehydes is oxidized to OH group in these reactions.



**(7) Give the reactions of aldehyde with Tollen's reagent**

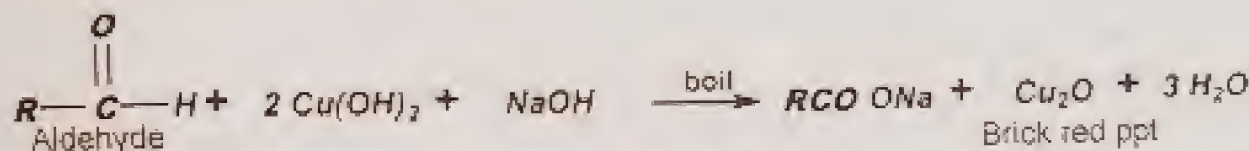
- Aldehydes form silver mirror with Tollen's reagent (ammonical silver nitrate solution).
- Add Tollen's reagent to an aldehyde solution in a test tube and warm.
- A silver mirror is formed on the inside of the test tube.





What types of ppt. are formed when aldehyde reacts with Fehling's solution

- Aliphatic aldehydes form a brick-red precipitate with Fehling's solution.
- To an aldehyde solution, add Fehling's solution and boil.
- A brick-red precipitate of cuprous oxide is formed.
- Ketones do not give this test.



## KEY POINTS

- Primary alcohols can be oxidized to aldehydes (or further to carboxylic acids).
- Secondary alcohols can be oxidized to ketones.
- Tertiary alcohols cannot be oxidized (no carbinol C-H).
- The protonation of a carbonyl gives a structure that can be redrawn in another resonance form that reveals the electrophilic character of the C since it is a carbocation.
- Organolithium or Grignard reagents react with the carbonyl group, C=O, in aldehydes or ketones to give alcohols.
- The carbonyl group, -C=O, is present in aldehydes and ketones. In aldehydes it is in a terminal position in the carbon chain. In ketones it is in a non-terminal position.
- Aldehydes and ketones are named using the suffixes -al and -one, respectively.
- Aldehydes are prepared by oxidising primary alcohols, ketones by oxidising secondary alcohols.
- The carbonyl group readily undergoes nucleophilic addition. This is sometime followed by the elimination of a molecule of water, resulting in a condensation reaction.
- Aldehydes are generally more reactive than ketones.
- The tendency of aldehydes to undergo nucleophilic addition makes them polymerize readily.
- Aldehydes can be oxidized to carboxylic acids by a variety of reagents. Ketones are not readily oxidized.
- The carbonyl group activates the hydrogen atoms on neighbouring carbon atoms, making them more readily substituted than those in alkanes.

## EXERCISE

**Q1: Select the right answer from the choices given with each question.**

- The carbon atom of a carbonyl group is  
 (a) sp hybridized (b) sp<sup>2</sup> hybridized (c) sp<sup>3</sup> hybridized (d) none of these
- Ketones are prepared by the oxidation of  
 (a) Primary alcohol (b) Secondary alcohol (c) Tertiary alcohol (d) none of these
- Acetone reacts with HCN to form a cyanohydrin. It is an example of  
 (a) Electrophilic addition (b) Electrophilic substitution  
 (c) Nucleophilic addition (d) Nucleophilic substitution
- Cannizzaro's reaction is not given by  
 (a) Formaldehyde (b) Acetaldehyde (c) Benzaldehyde (d) Trimethylacetaldehyde
- Which of the following reagents will react with both aldehydes and ketones?  
 (a) Grignard reagent (b) Tollen's reagent (c) Fehling's reagent (d) Benedict's reagent
- Aldehydes are the oxidation product of  
 (a) p-alcohols (b) s-alcohols (c) ter-alcohols (d) carboxylic acids
- Which of the following compounds will not give iodoform test on treatment with I<sub>2</sub>/NaOH.  
 (a) Acetaldehyde (b) Acetone (c) Butanone (d) 3-pentanone
- Aldehydes and ketones are carbonyl compounds. Which of them react both with NaBH<sub>4</sub> and with Tollen's reagent.  
 (a) Both aldehydes and ketones (b) Aldehydes only







100

[illegible]
$$\frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} f(x) \delta(x-a) dx = f(a)$$
$$\frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} f(x) \delta(x-a) dx = f(a)$$

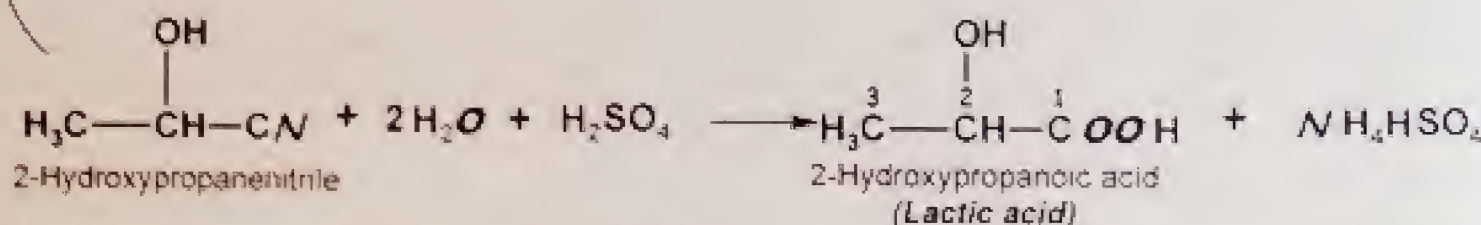
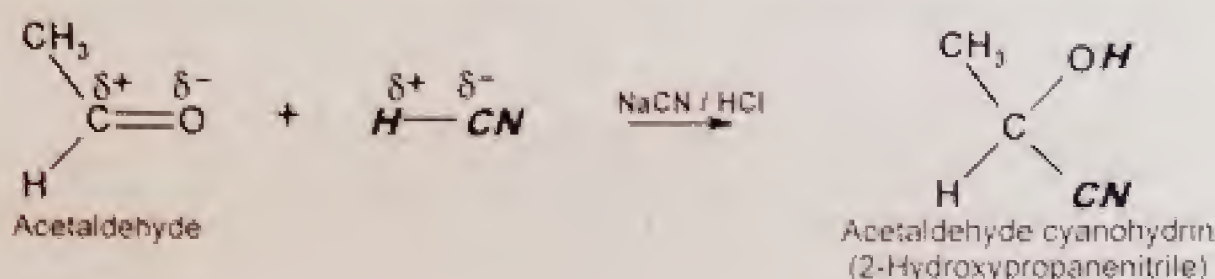
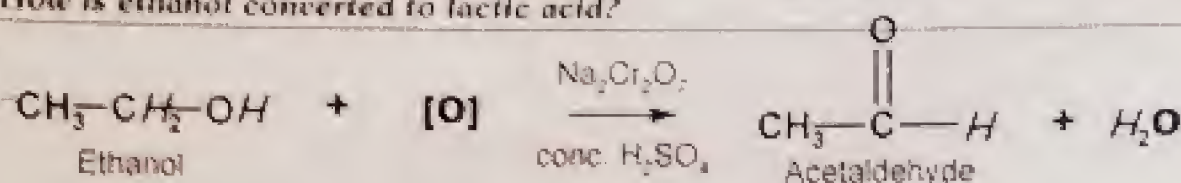
$$= \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-t^2} dt = \frac{1}{\sqrt{\pi}}$$
$$\frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} f(x) e^{-x^2} dx = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} f(x) e^{-x^2} dx$$
[illegible][illegible][illegible]



(iii) What is the mechanism of HCN addition to carbonyl compounds?

Page 321

(iv) How is ethanol converted to lactic acid?

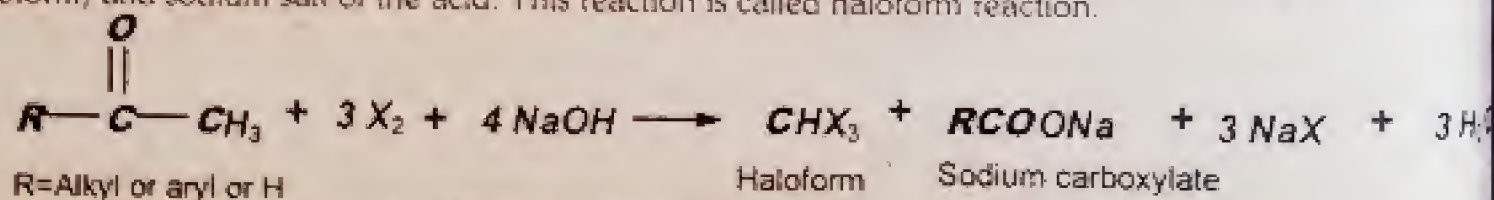


(v) What is the addition product of Grignard reagent to formaldehyde, acetaldehyde and ketone?

Page 322

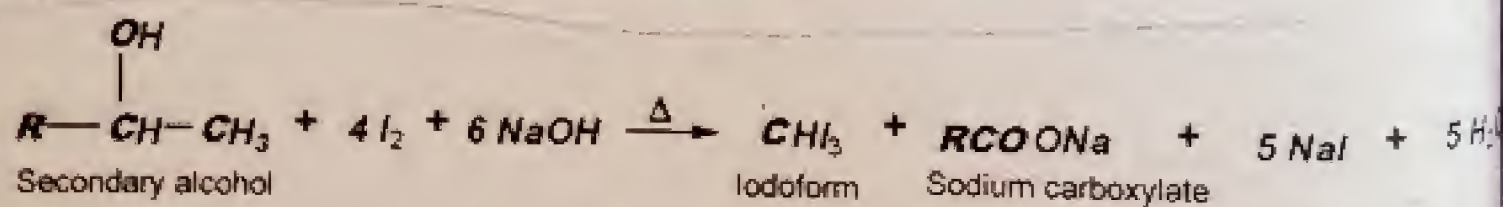
(vi) What is Haloform reaction?

Acetaldehyde, ethanol, methyl ketones and secondary alcohols with methyl group at  $\alpha$ -carbon, react with halogens ( $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ) in the presence of sodium hydroxide to give haloform (chloroform, bromoform, iodoform) and sodium salt of the acid. This reaction is called haloform reaction.

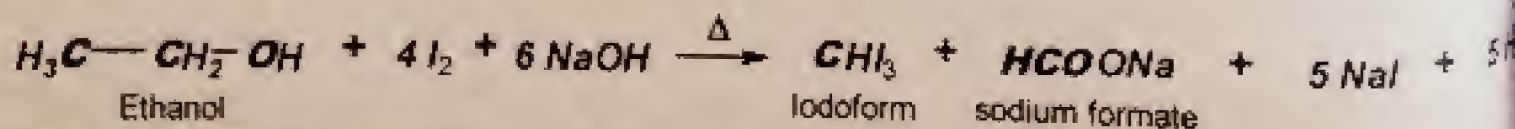


(vii) Which type of alcohols undergo iodoform reaction?

Secondary alcohols containing the methyl group also undergo this reaction.



Ethanol is the only primary alcohol that gives this reaction.



(viii) How are methanol and ethanol polymerized?



(ix) Why formaldehyde do not give aldol condensation reaction?

For aldol condensation reaction, the carbonyl compound must have  $\alpha$ -hydrogen (hydrogen attached to the carbon atom next to carbonyl group). In formaldehyde, there is no  $\alpha$ -hydrogen so it cannot give aldol condensation reaction.

(x) Give the mechanism of addition of sodium bisulphate to ketones.

Page 323

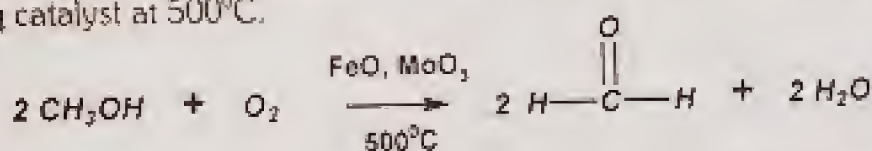
**Q3: Give detailed answers for the following questions.**

(i) What is the reactivity of the carbonyl group?

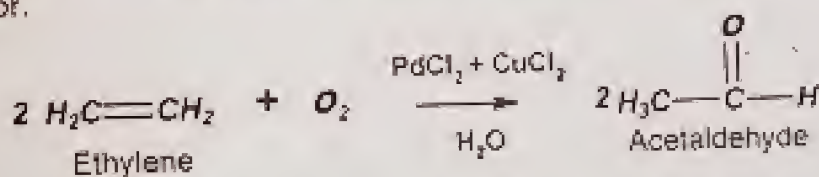
Page 319

(ii) How will you prepare formaldehyde and acetaldehyde on industrial scale?

In industry, formaldehyde is prepared by passing a mixture of methanol vapours and air over iron oxide - molybdenum oxide or Ag catalyst at  $500^\circ\text{C}$ .

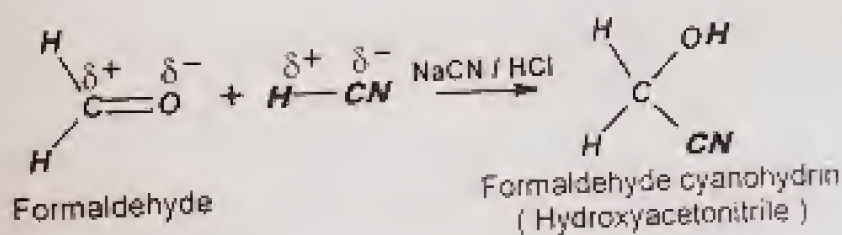


In industry, acetaldehyde is prepared by oxidation of ethylene in air using palladium chloride catalyst with cupric chloride promotor.



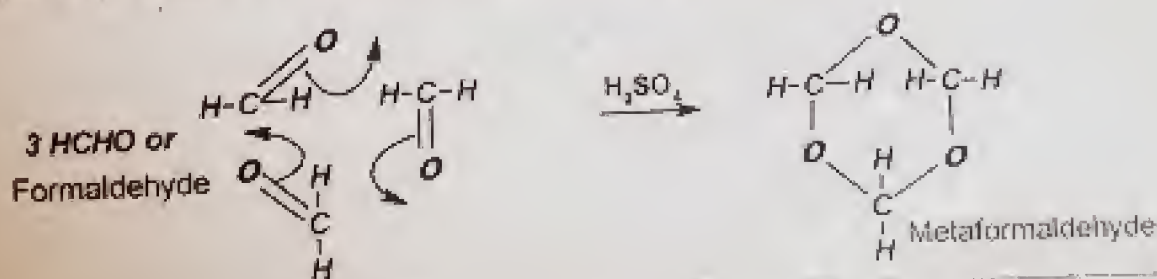
(iii) How formaldehyde reacts with following?

(a) HCN

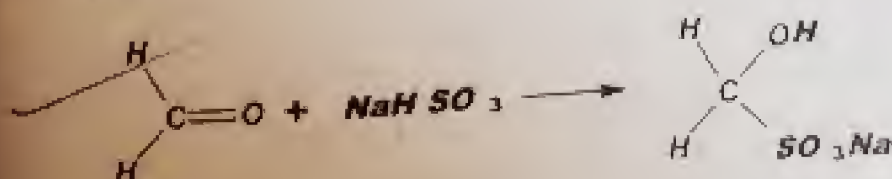


(b)  $\text{H}_2\text{SO}_4$

Formaldehyde polymerizes in the presence of dil.  $\text{H}_2\text{SO}_4$  to give metaformaldehyde.

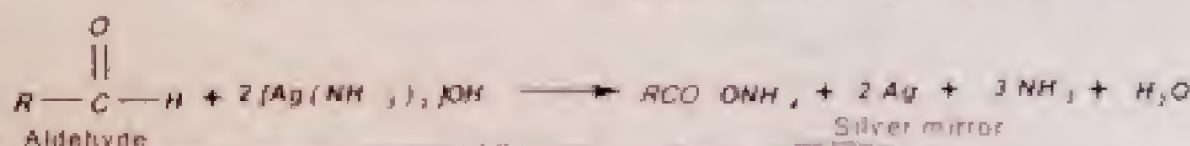


(c)  $\text{NaHSO}_3$

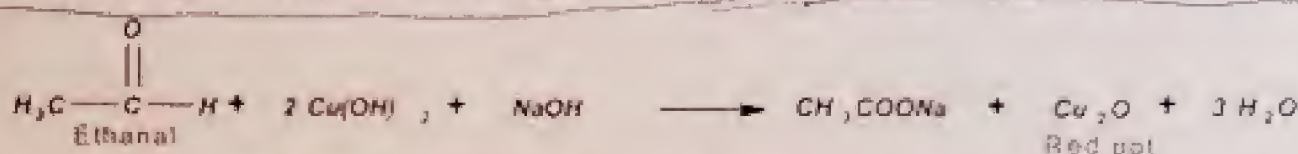




- (i) Define and explain aldol condensation along with mechanism.  
Page 324
- (ii) Give detail of haloform reaction. Why it is called so?  
Page 327
- (iii) Give the following reductions of aldehydes and ketones along with mechanism.  
(a)  $\text{NaBH}_4$ , (b) Catalytic reduction  
Page 333
- (iv) What is the mechanism for addition of ammonia derivatives to carbonyl group?  
Page 330
- (v) Which type of aldehydes give Cannizzaro's reaction? Explain with mechanism.  
Page 326
- (vi) How do you distinguish a ketone and an aldehyde by chemical method?  
Aldehydes gives silver mirror with Tollen's reagent while ketone does not.

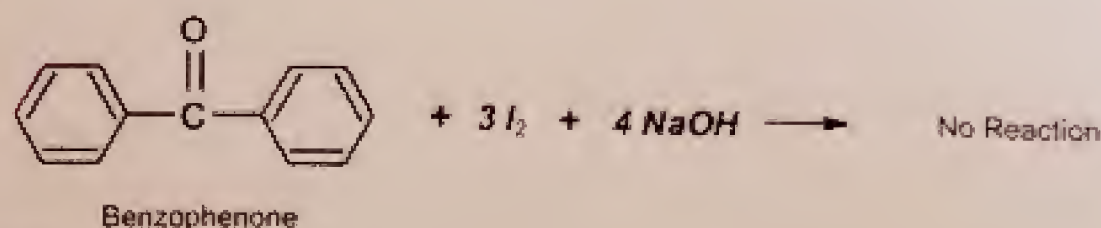
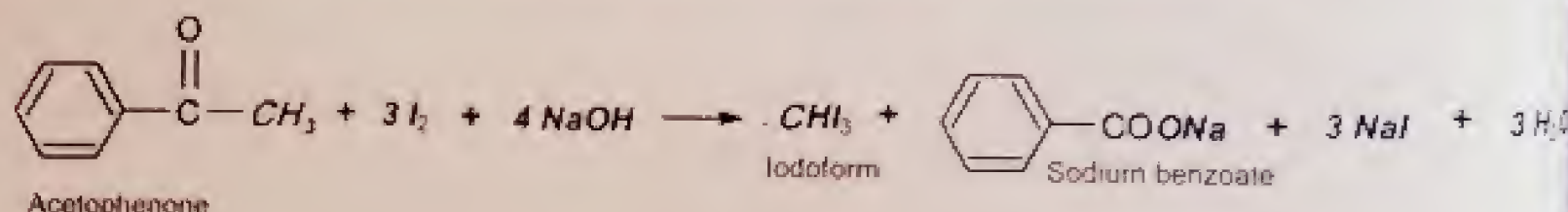


Aldehydes gives red ppt with Fehling's solution and Benedict's solution while ketones does not



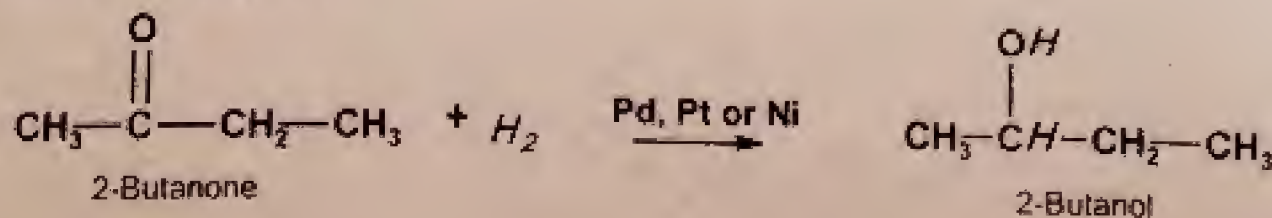
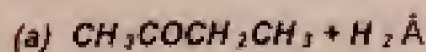
- (vii) How will you differentiate between acetophenone and benzophenone?

Acetophenone is a methyl ketone, so it will give iodoform test while benzophenone will not give iodoform

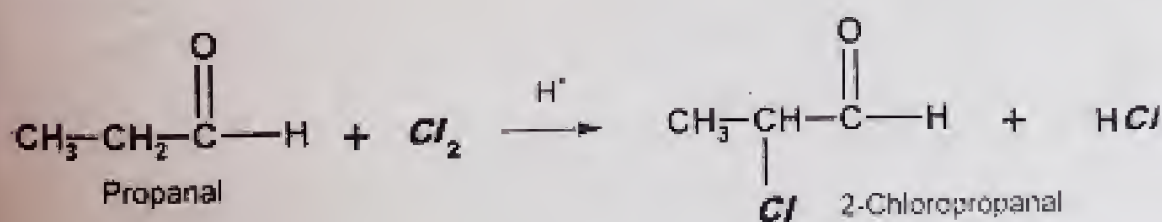
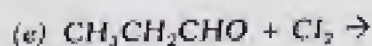
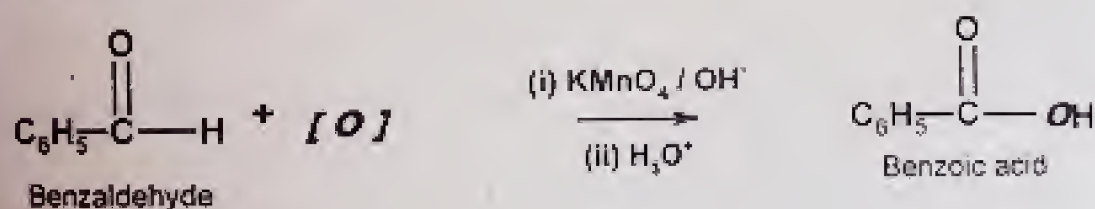
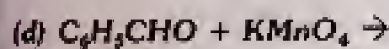
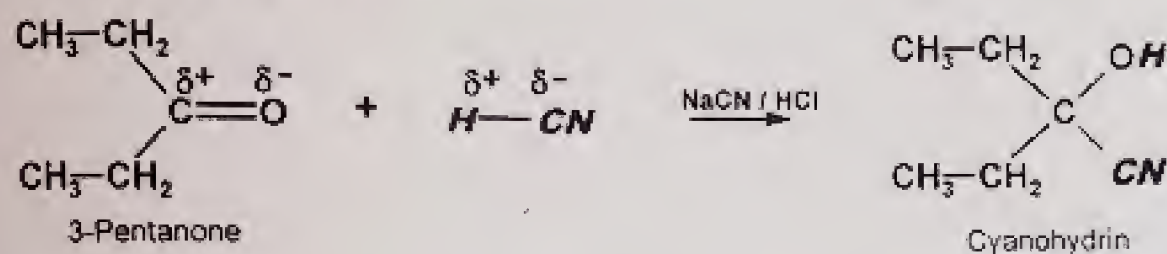
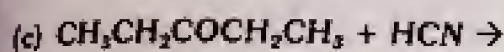
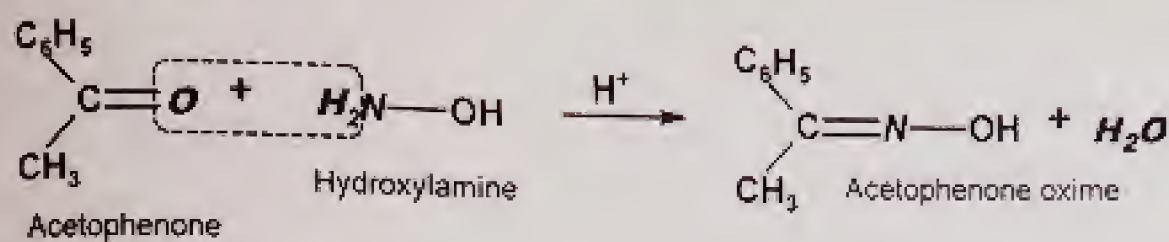
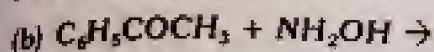


test.

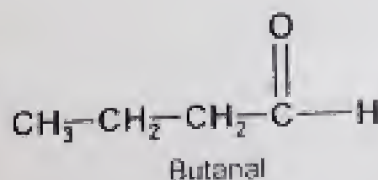
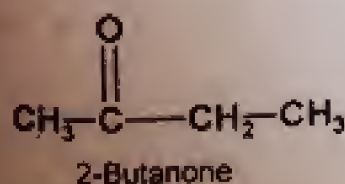
- (viii) Predict the formulas of the products of the following reaction







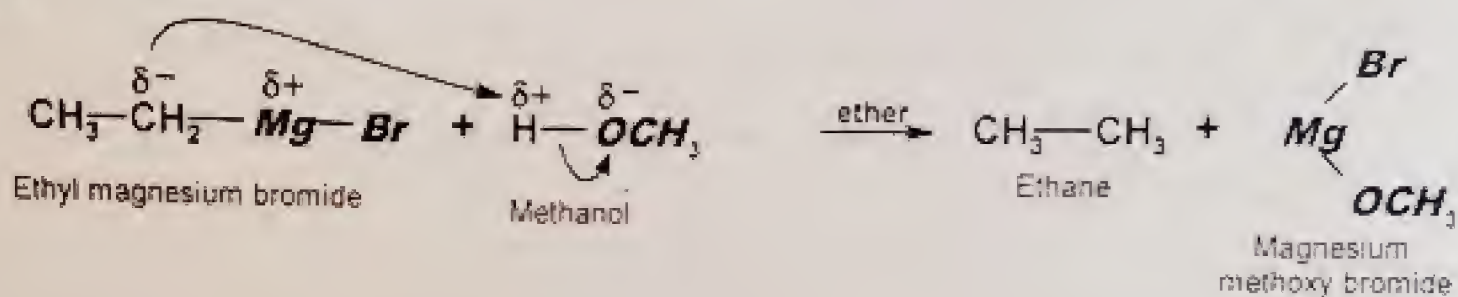
(xli) Write structural formulas for all compounds of molecular formula  $C_4H_8O$  containing a carbonyl group.



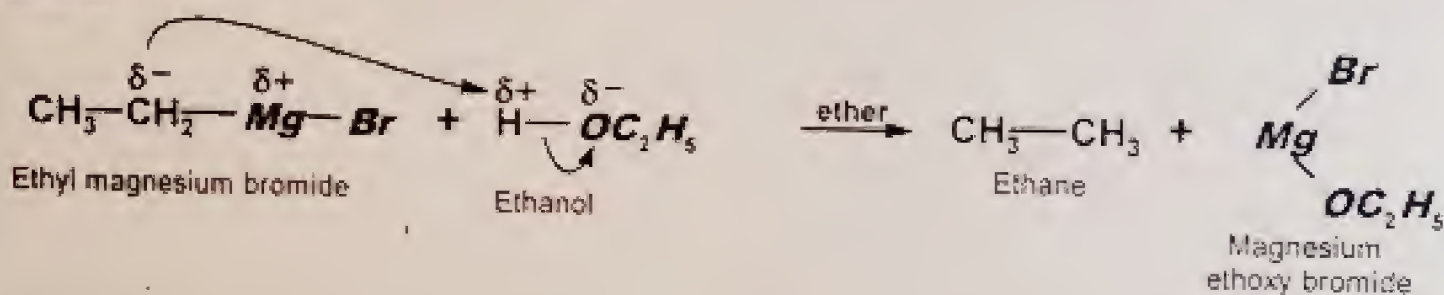


(xiii) Predicts the formulas of the compounds formed when the following are treated with the Grignard's reagent methyl magnesium bromide, followed by water.

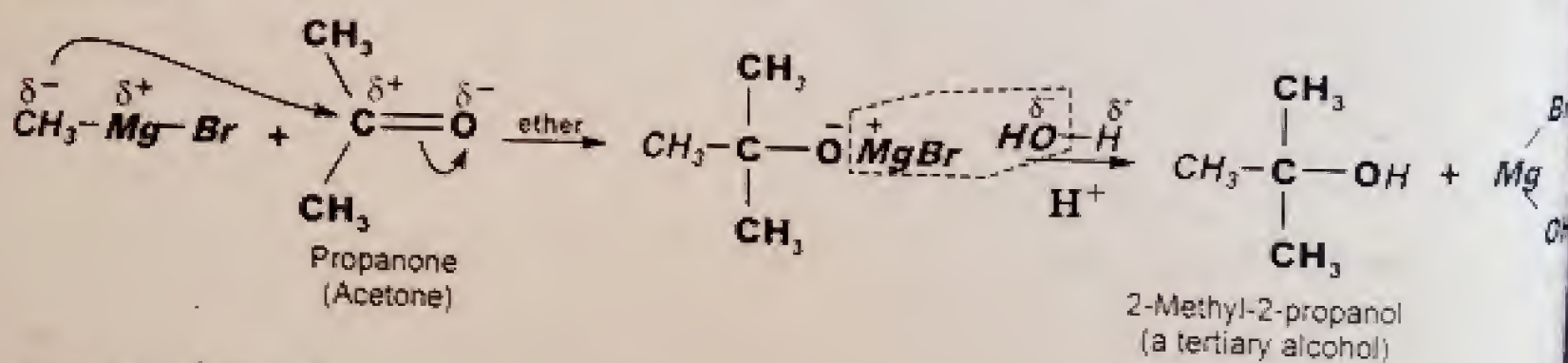
**Methanol**



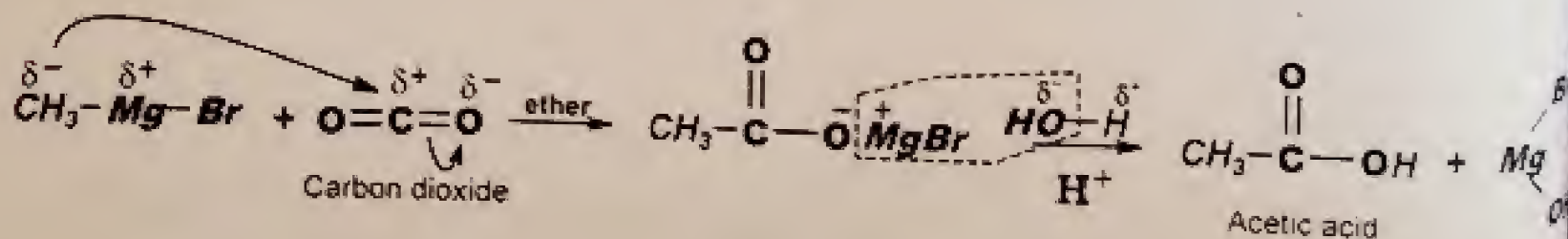
**Ethanol**



**Propanone**



**Carbon dioxide**





TEST YOUR SKILLS

Marks: 85

OBJECTIVE

Time: 20 Minutes

Marks: 17

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Q1. Circle the correct option i.e. A/B/C/D. Each part carries one mark.

- The carbon in carbonyl group is  
A.  $sp^3$  B.  $sp^2$  C.  $sp$  D. Different in different conditions
- The name of formaldehyde in IUPAC system is  
A. Ethanol B. Methanol C. Methanal D. None of above
- Formalin is  
A. 40% solution of  $CH_3CHO$  in water B. 60% solution of  $CH_3CHO$  in acetone  
C. 40% solution of HCHO D. 75% solution of phenol
- Which one of the following cannot give cannizzaro's reaction  
A. Formaldehyde B. Acetaldehyde C. Benzaldehyde D. Trimethylacetaldehyde
- Aldehydes are more reactive than ketones because  
A. steric hindrance B. Electronic reason C. Both 'a' and 'b' D. None
- A cannizzaro's reaction takes place  
A. With same molecule of aldehyde B. With different molecule of aldehydes  
C. With same and different aldehydes D. With neither
- Catalysts used for the preparation of formaldehyde is  
A. Pt-asbestos B.  $FeO, MoO_3$  C. Cu catalyst D. All of above
- Aldol condensation is not successful with compounds  
A. Having no  $\alpha$ -hydrogen B. Having  $\alpha$ -hydrogen C. Having  $\alpha$ -methyl group D. None
- Polymer of formaldehyde is called  
A. Meta formaldehyde B. Paraldehyde C. Both 'a' and 'b' D. None
- Tollen's test is used for the detection of  
A. Aldehydes only B. Ketones only C. Carboxylic acids only D. Aldehydes and ketones
- Aldol condensation is  
A. Electrophilic B. Base catalyzed C. Both D. None
- Which of the following does not give iodoform reaction?  
A.  $CH_3CH_2OH$  B.  $CH_3OH$  C.  $CH_3CHO$  D.  $PhCOCH_3$
- Phenylhydrazine on treatment with carbonyl group form  
A. Phenyl hydrazones B. Hydroxyl amines C. Oximes D. None
- acetals and ketals are formed by reaction of carbonyl compounds with  
A. Acids B. Alcohols C. Phenols D. Esters
- Paraldehyde is a polymer of  
A. Acetaldehyde B. Formaldehyde C. Propionaldehyde D. None of these
- Isopropanal on treatment with  $CrO_3$  at  $300^\circ C$  forms  
A. Acetone B. Acetaldehyde C. Ethane D. Propylene
- Which one of the following can undergo Aldol condensation reaction  
A. Formaldehyde B. Acetaldehyde C. Benzaldehyde D. Trimethylacetaldehyde

SUBJECTIVE

Total Marks Section B and C: 68

Time: 2:35 Hours

Section - B (Marks 42) ( $14 \times 3 = 42$ )

Q2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines.

- The reactions in which two molecules combine to form new compounds with or without elimination of a small molecule is called Condensation. 01
  - What type of condensation will be shown by the following:  
A.  $CH_3CHO$  B.  $C_6H_5CHO$  02
  - Write chemical equation along with mechanism for the conversion of  $CH_3CHO$  into products. 02
- Why the aldehydes with no  $\alpha$ -hydrogen give Cannizzara's reaction? 1.5
  - Distinguish between benzaldehyde and acetaldehyde. 1.5
- Show with the help of mechanism how acetaldehyde in the presence of strong base gives crotonaldehyde 03
- Write the formula of 2,4 - Dinitrophenyl hydrazine and Semicarbazide 01
  - Give the mechanism of the reaction between formaldehyde and hydrazine 02



CH # 19: Aldehydes and Ketones

- (v) Give a reaction example of disproportionation reaction of aldehyde 03
- (vi) Give a general mechanism for the base-catalysed nucleophilic addition reaction of carbonyl compounds. 03
- (vii) a. What is Tollen's test? Also give the reaction 02  
b. Convert acetone  $\rightarrow$  acetone hydrazone. 01
- (viii) a. Briefly explain the reactivity of carbonyl group. 1.5  
b. How can acetaldehyde be prepared by the dry distillation of a mixture having calcium salt of formic and acetic acid 1.5
- (ix) a. What is the difference between an aldehyde and ketone? 01  
b. What is formalin. How it can be obtained? 02
- (x) a. Discuss the reactivity of carbonyl group. 1.5  
b. What type of reactions aldehydes and ketones usually under go 1.5
- (xi) a. How  $\alpha$ -hydroxy acids are obtained from aldehydes and ketones? 1.5  
b. What is a haloform reaction? Give one example.
- (xii) a. What kind of aldehydes and ketones give aldol condensation gives an example of each? 01  
b. What kind of aldehydes give cannizzaro's reaction? 01  
c. Which aldehydes and ketones give haloform reactions? 01
- (xiii) a. What are acetals and how are they formed? 02  
b. Why ketones do not undergo oxidation easily? 01
- (xiv) a. Distinguish between ethanol and Propanone by a chemical test. 1.5  
b. How will you distinguish between ethanal and propanal? 1.5
- (xv) a. Describe briefly the mechanism of acid catalysed nucleophilic addition to a carbonyl compound? 02  
b. What is Fehling's solution test? Give chemical equation. 01
- (xvi) a. Give three industrial uses of formaldehyde. 1.5  
b. Give three industrial uses of Acetaldehyde. 1.5
- (xvii) a. Give the mechanism of addition of addition of HCN to Acetone? 02  
b. Write the applications of Iodoform test? 01
- (xviii) a. Why formaldehyde do not give aldol condensation reaction? 01  
b. Give general mechanism of addition of phenyl hydrazine to acetaldehyde? 02
- (xix) a. How may acetaldehyde be prepared on industrial scale? 02  
b. What is Benedict solution test? 01

Section - C

**Note:** Attempt any TWO questions. All questions carry equal marks. ( $2 \times 13 = 26$ )

- Q. 3.** a. How will you prepare formaldehyde on industrial scale? 03  
b. What is Cannizzaro's reaction? Write its mechanism 03  
c. How formaldehyde reacts with following 03  
(i) HCN (ii)  $H_2SO_4$  (iii)  $NaHSO_3$   
d. Define and explain aldol condensation along with mechanism. 05
- Q. 4.** a. Write mechanisms of the following reactions 04  
(i) Cannizzaro's reaction.  
(ii) Addition of sodium bisulphite to acetone. 05  
b. How does acetaldehyde react with the following 05



- 03

- 03

12

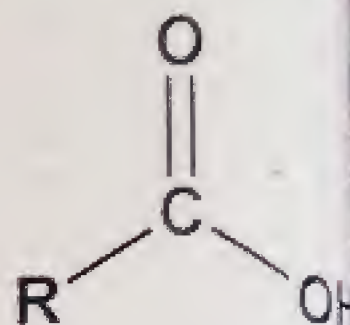
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- 02



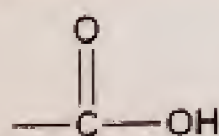
## CHAPTER # 20

# CARBOXYLIC ACIDS AND FUNCTIONAL DERIVATIVES



## INTRODUCTION

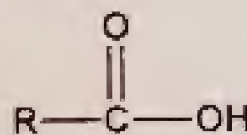
- Organic compounds which contain functional group in their molecule are called carboxylic acids.



- Aliphatic carboxylic acids have the carboxyl group attached with an open chain of carbon atoms. They may be represented by the general formula



Or



where R = H or any alkyl group

- There are organic compounds which contain more than one carboxylic groups in their molecule. Thus dicarboxylic acids and tricarboxylic acids etc. are formed.

## NOMENCLATURE

### Common Names

- Many carboxylic acids are known by their common names.
- The positions of other groups attached with the chain containing the carboxyl group are indicated by the Greek letters  $\alpha$ ,  $\beta$  etc.
- The carbon adjacent to the carboxylic group is called the  $\alpha$  (alpha) carbon. The carbon atom in the carboxyl group is not the  $\alpha$  carbon e.g.

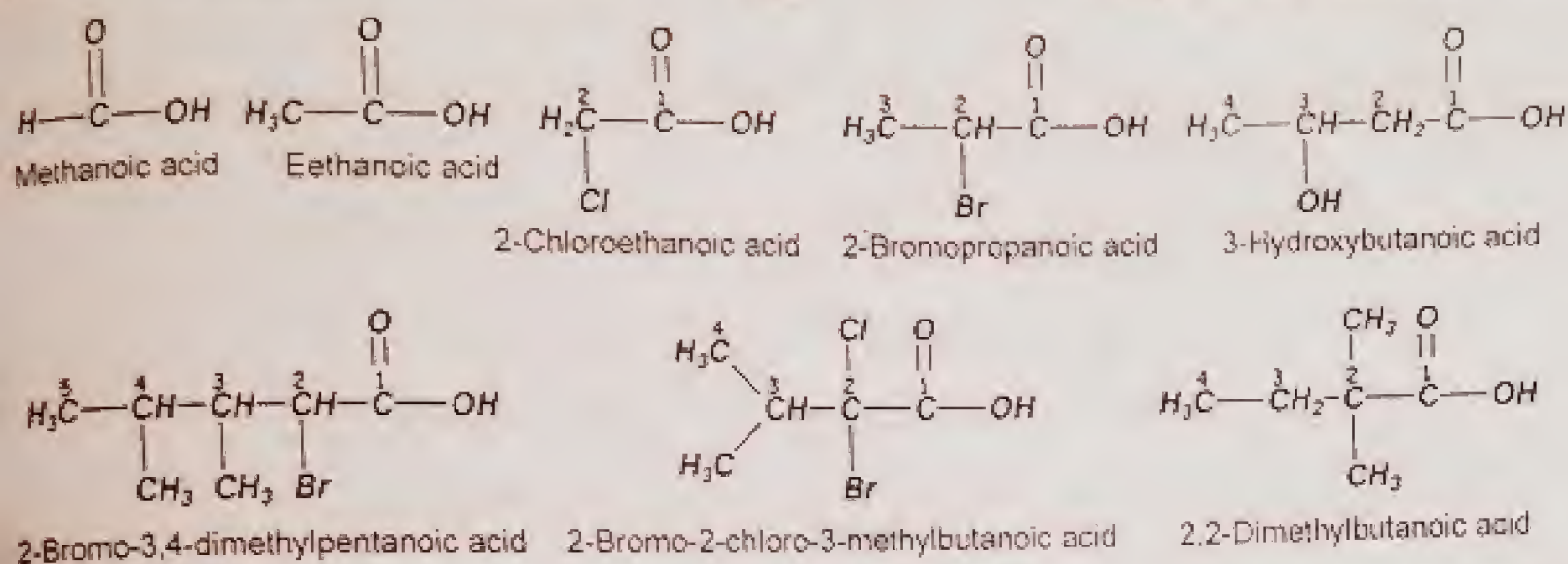


### The IUPAC System

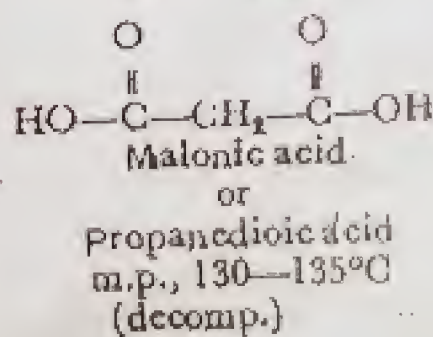
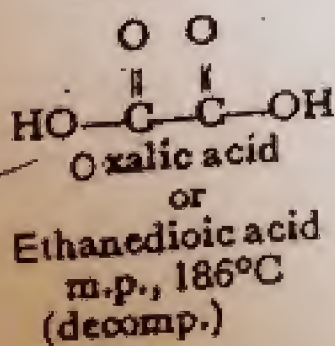
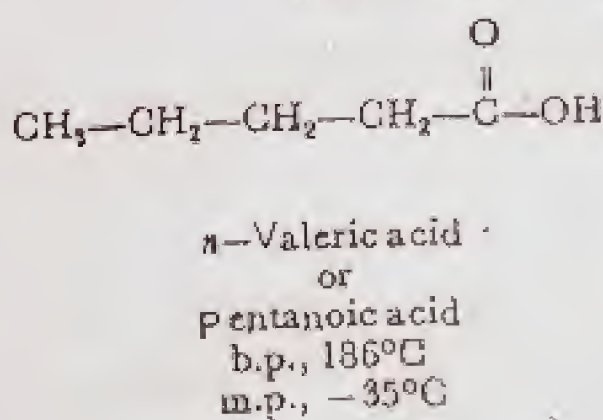
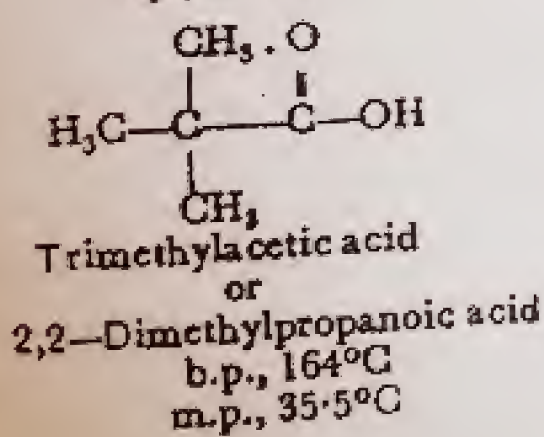
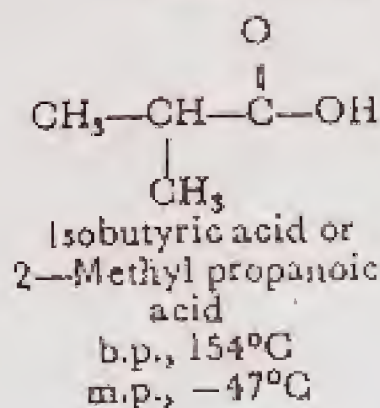
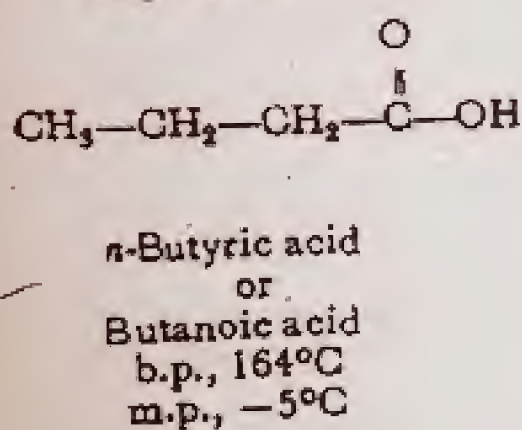
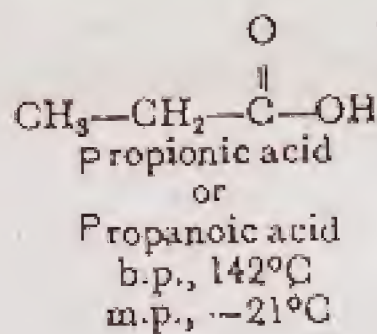
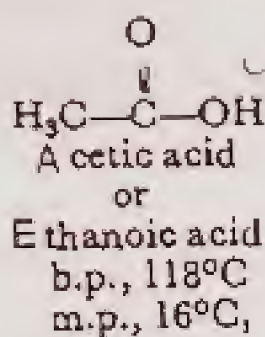
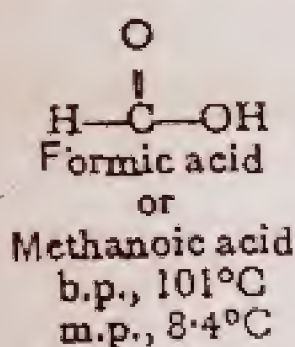
#### Aliphatic Carboxylic Acids

- Select the longest carbon chain containing the carboxyl group.
- Change the 'e' of the corresponding alkane to 'oic acid'.
- Numbering of the carbon begins with the carbon of the carbonyl group.
- Since the carboxyl group is always present at one end, therefore its position is not mentioned.
- Substituents are also named and their position is indicated.

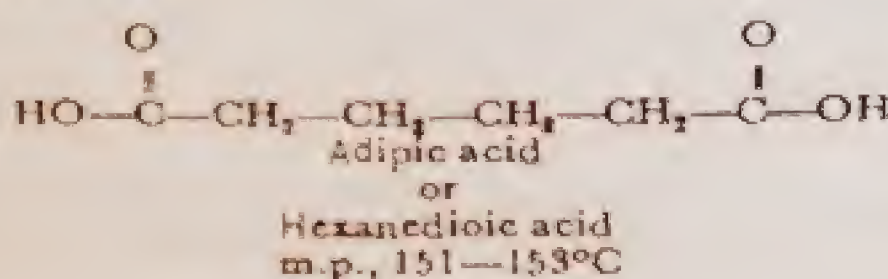
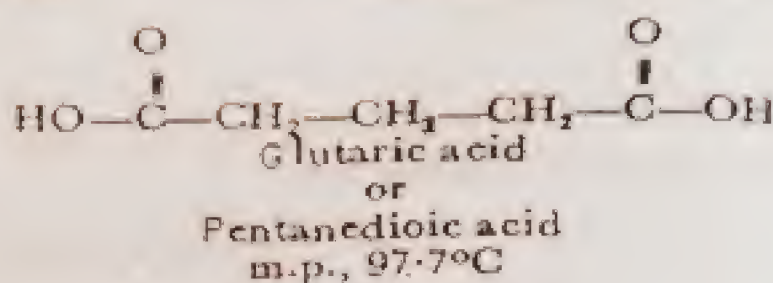
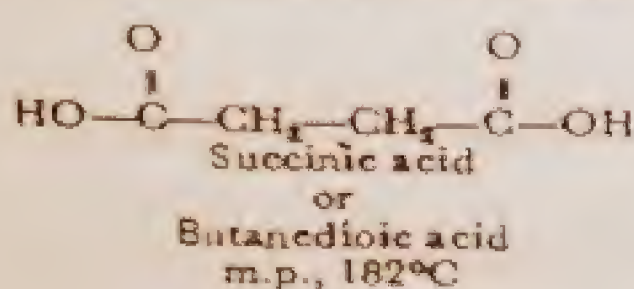




The names and the structural formulas of a few carboxylic acids are given below. Boiling points and melting points are also given.

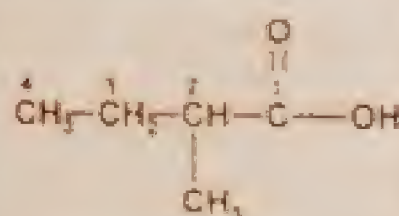




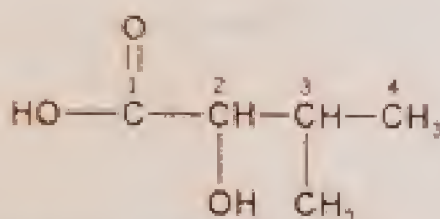


Note that the dicarboxylic acids are named in the IUPAC system by adding dioic acid to the name of the alkane containing the same number of carbon atoms as the carbon chain containing the two carboxyl groups.

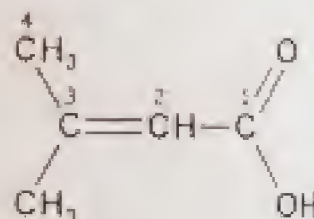
### MORE PRACTICE



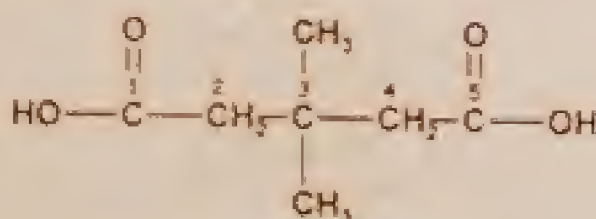
2-Methylbutanoic acid



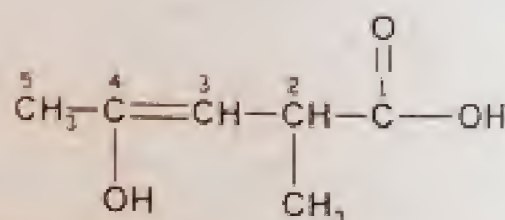
2-Hydroxy-3-methylbutanoic acid



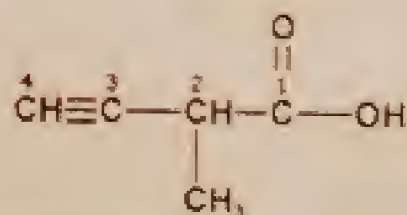
3-Methyl-2-butenic acid



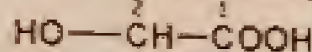
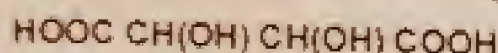
3,3-Dimethylpentanedioic acid



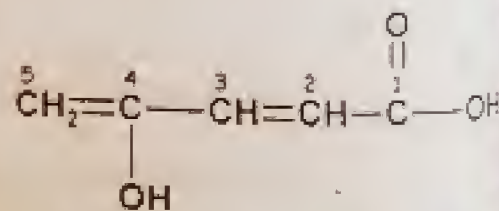
4-Hydroxy-2-methyl-3-pentenoic acid



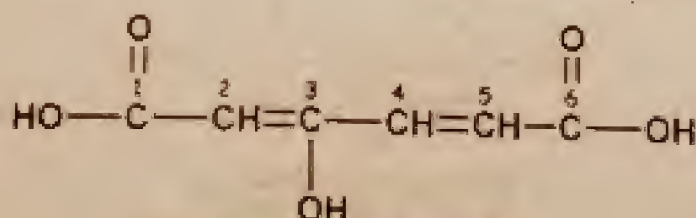
2-Methyl-3-butyric acid



2,3-Dihydroxybutanedioic acid



4-Hydroxypenta-2,4-dienoic acid



3-Hydroxyhexadienedioic acid



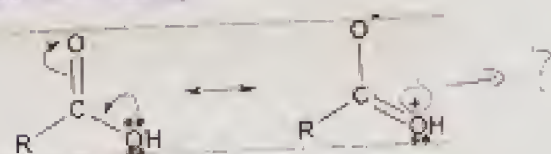
## PHYSICAL PROPERTIES:

The C=O and O-H groups are polar due to the electronegativity difference of atoms. The polar nature of both the O-H and C=O bonds results in the formation of strong hydrogen bonds with other carboxylic acid molecules or other H-bonding systems (e.g. water). The results are:

- higher melting and boiling points compared to similar alcohols
- high solubility in aqueous media
- hydrogen bonded dimers in gas phase and dimers or aggregates in pure liquid

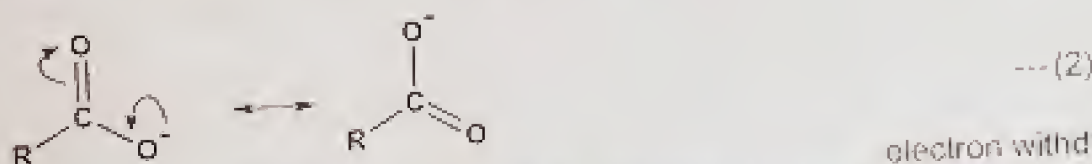
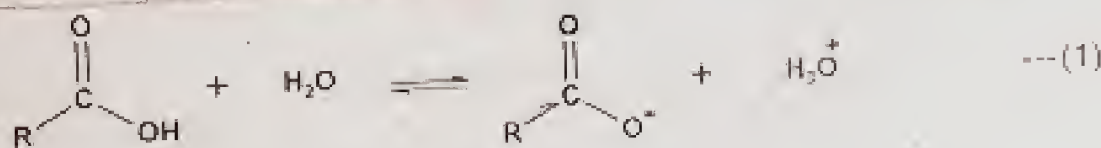
## STRUCTURE:

- The COOH unit is planar and consistent with  $sp^2$ -hybridization.
- There is a resonance interaction of the lone pairs of the hydroxyl oxygen with the  $p$  system of the carbonyl as shown in the figure.



## ACIDITY:

- Carboxylic acids are the most acidic simple organic compounds ( $pK_a \sim 5$ ) compared with alcohols ( $pK_a \sim 16$ ). Remember, the lower the  $pK_a$ , the stronger the acid. The acidity depends upon (i) ease of donation of proton (ii) stability of carboxylate anion. More ease of donation and greater stability of anion, stronger the acid. However, they are only weak acids compared to mineral acids like HCl or  $H_2SO_4$ .
- The carboxylate ion is stabilized due to resonance (eq. 2). The delocalization of negative charge takes place between two electronegative oxygen atoms.



- Adjacent substituents increase the acidity because they withdraw negative charge and thus further stabilize the carboxylate anion.

Carboxylic Acid	Structure	$pK_a$	Carboxylic Acid	Structure	$pK_a$
Ethanoic acid	$CH_3CO_2H$	4.7	Dichloroethanoic acid	$CHCl_2CO_2H$	1.3
Propanoic acid	$CH_3CH_2CO_2H$	4.9	Trichloroethanoic acid	$CCl_3CO_2H$	0.9
Fluoroethanoic acid	$CH_2FCO_2H$	2.6	Nitroethanoic acid	$O_2NCH_2CO_2H$	1.7
Chloroethanoic acid	$CH_2ClCO_2H$	2.9			

## PREPARATIONS OF CARBOXYLIC ACIDS

### Summary

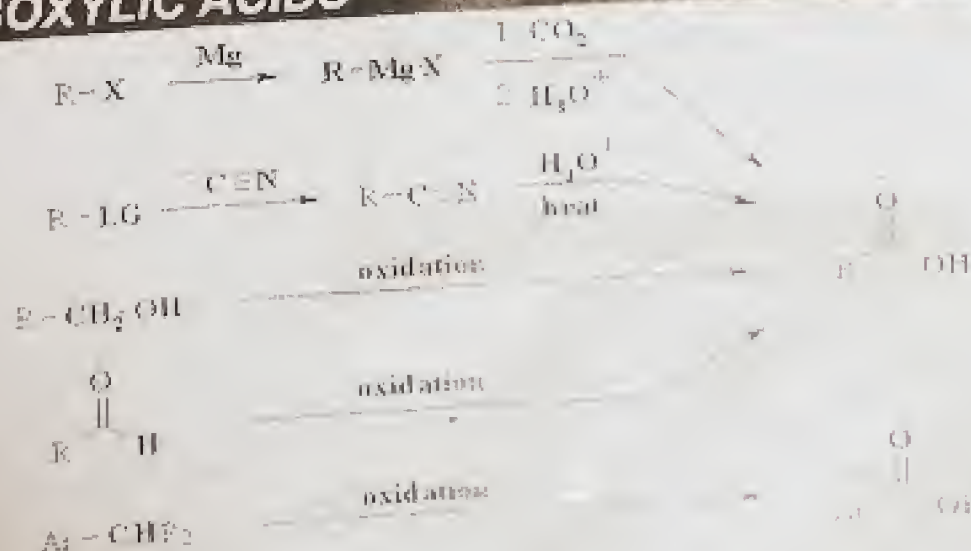
Carbonation of Grignards

Hydrolysis of Nitriles

Oxidation of  $1^\circ$  Alcohols

Oxidation of Aldehydes

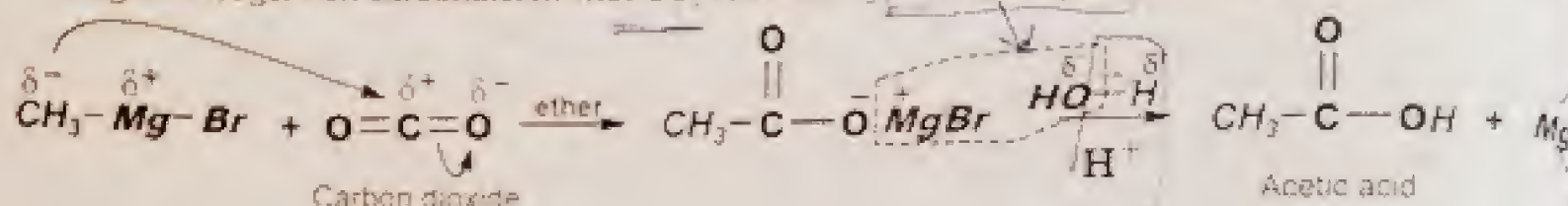
Oxidation of Alkyl Benzenes





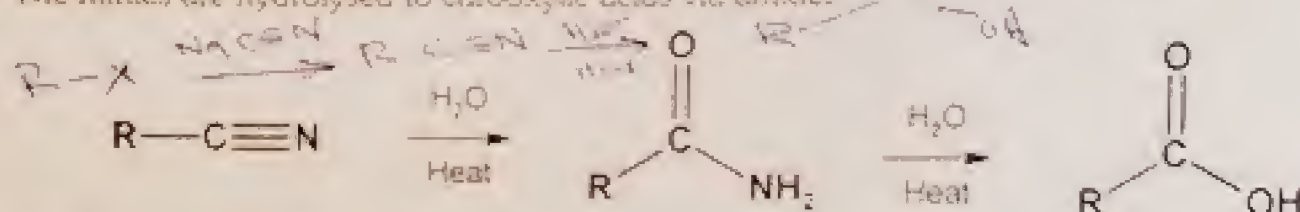
### (1) CARBONATION OF GRIGNARD REAGENTS, $RMgX$ , BY $CO_2$

Grignard reagent on carbonation with  $CO_2$  followed by acid hydrolysis gives carboxylic acid



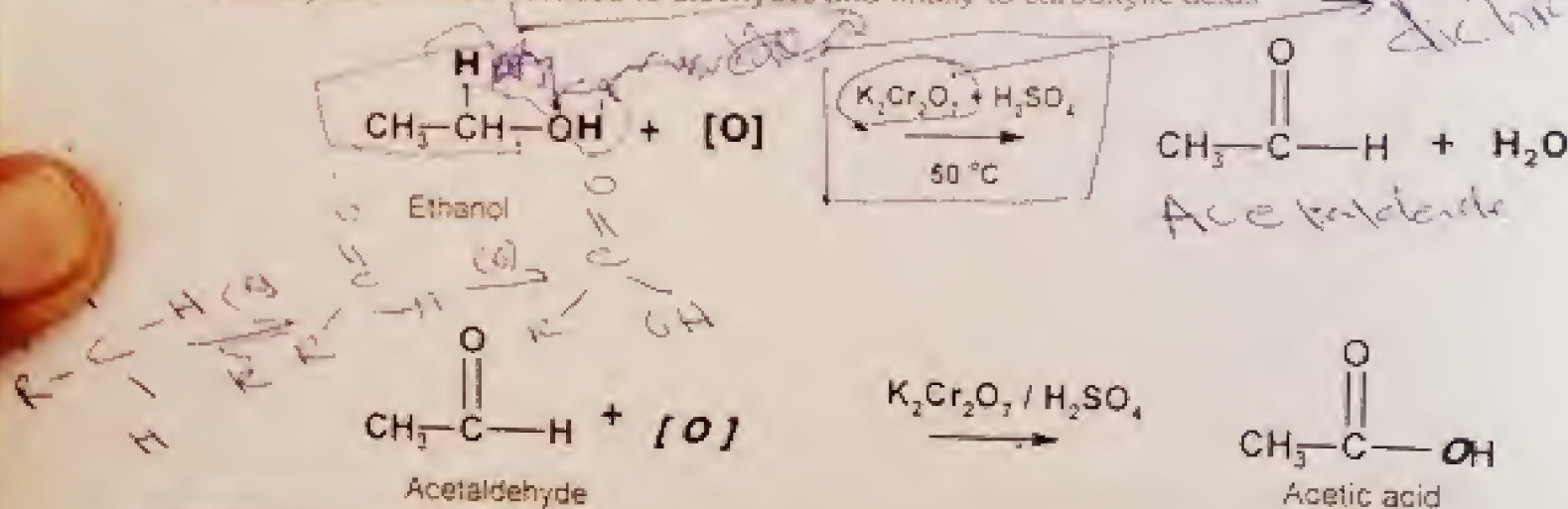
### (2) HYDROLYSIS OF NITRILES

The nitriles are hydrolysed to carboxylic acids via amides



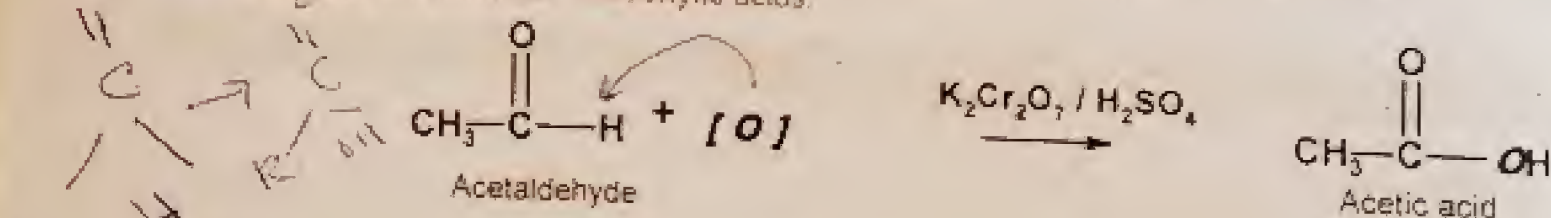
### (3) OXIDATION OF PRIMARY ALCOHOLS

Primary alcohols are oxidized to aldehydes and finally to carboxylic acids



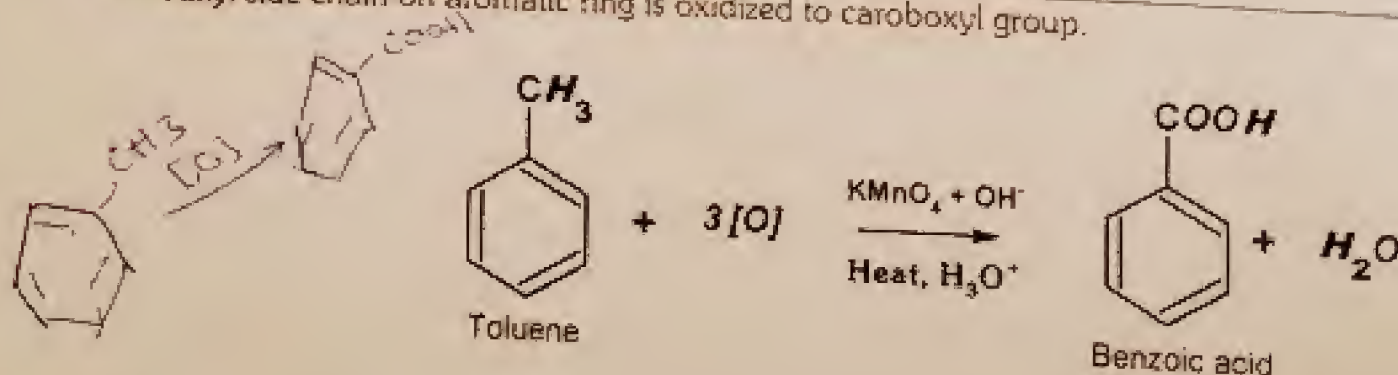
### (4) OXIDATION OF ALDEHYDES

Aldehydes are oxidized to carboxylic acids.



### (5) OXIDATION OF ALKYL BENZENES

Alkyl side chain on aromatic ring is oxidized to carboxyl group.





## REACTIVITY

- The carboxyl group shows the chemistry of both the carbonyl (C=O) and the hydroxyl (-OH) groups.
- In most reactions, the carboxyl group is retained.
- However the reactivity of these molecules is due to the presence of carbonyl group.

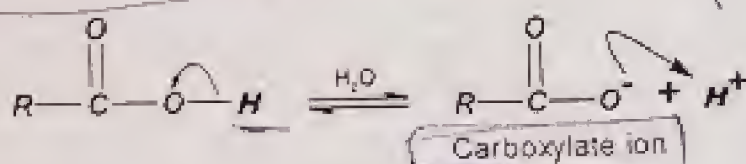
## REACTIONS OF CARBOXYLIC ACIDS

Carboxylic acids undergo the following types of reactions.

- The reaction in which hydrogen atom of the carboxyl group is involved (salt formation).
- The reaction in which OH group is replaced by another group.
- The reactions involving carboxyl group as a whole.

### (A) REACTION INVOLVING HYDROGEN ATOM OF THE CARBOXYL GROUP

Carboxylic acids are weaker acids than mineral acids. They produce  $H^+$  when dissolved in water.



In the presence of water ( $H_2O$ ), the proton breaks away as  $H_3O^+$  ion.

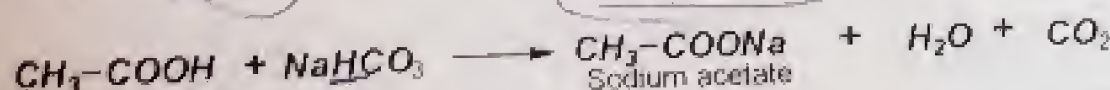
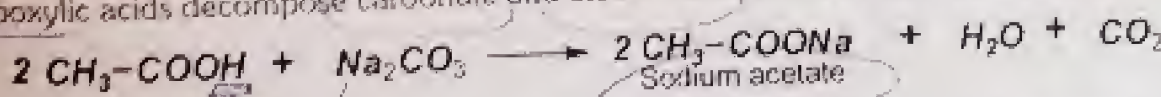
### (1) REACTIONS WITH BASES

Carboxylic acids react with bases (NaOH, KOH) to form salts



### (2) REACTION WITH CARBONATES AND BICARBONATES

Carboxylic acids decompose carbonate and bicarbonates evolving carbon dioxide gas with effervescence.



### (3) REACTIONS WITH METALS

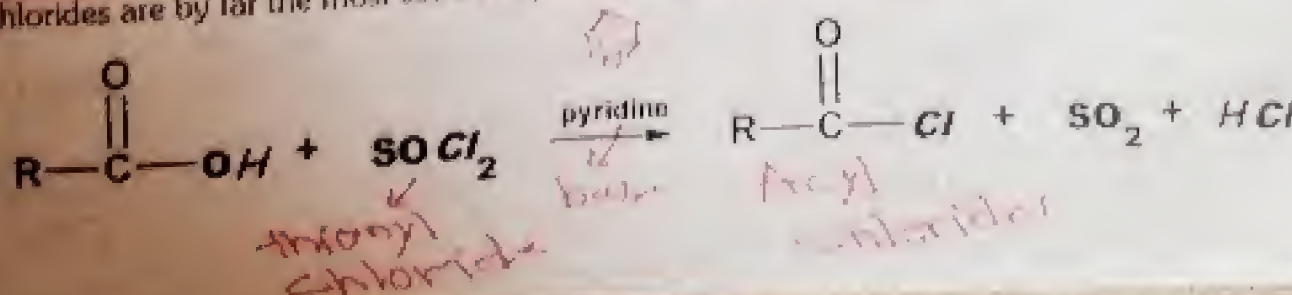
Carboxylic acids reaction with active metals such as Na, K, Ca, Mg etc. to form their salts with the evolution of hydrogen gas.



### (B) REACTION INVOLVING OH GROUP OF THE CARBOXYL GROUP

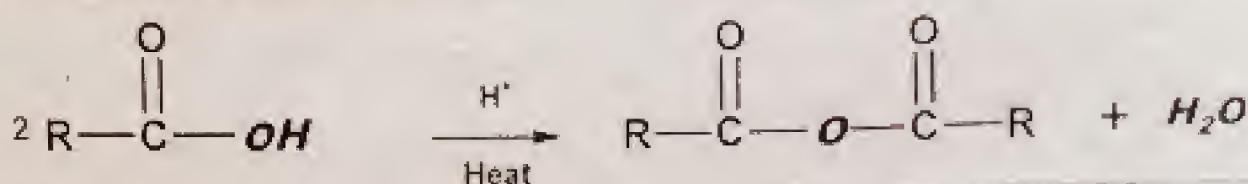
#### (1) PREPARATION OF ACYL CHLORIDES

- Acyl chlorides are prepared by treating the carboxylic acid with thionyl chloride,  $SOCl_2$ , in the presence of a base.
- Acyl chlorides are by far the most commonly encountered of the acyl halides.



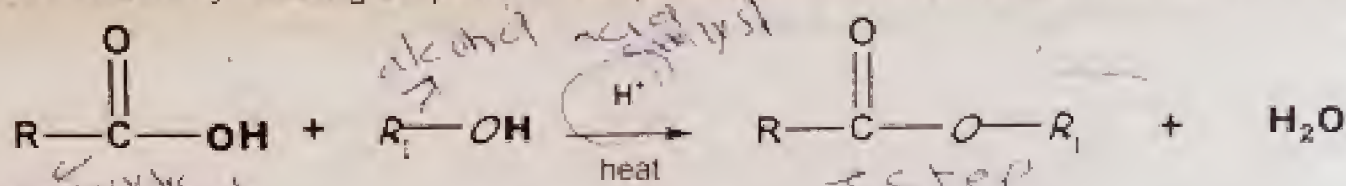


## (2) PREPARATION OF ACID ANHYDRIDES

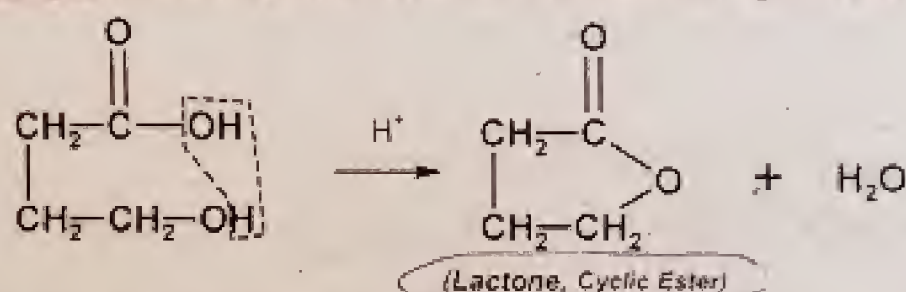


## (3) PREPARATION OF ESTERS

Esters are obtained by refluxing the parent carboxylic acid with the appropriate alcohol with an acid catalyst.



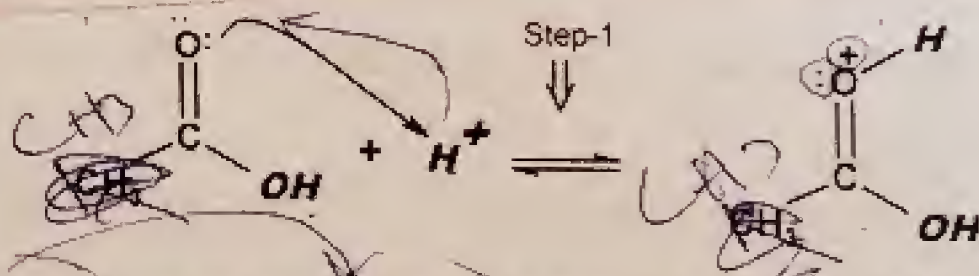
- This reaction is also known as the **Fischer esterification**.
- ✓ The equilibrium can be driven to completion by using an excess of either the alcohol or the carboxylic acid or by removing the water as it forms.
- Alcohol reactivity order is  $\text{CH}_3\text{OH} > 1^\circ > 2^\circ > 3^\circ$ . It is due to steric effects. Thus, larger the alkyl group, lesser the reactivity.
- ✓ Esters can also be made from other carboxylic acid derivatives, especially acyl halides and anhydrides, reacting them with the appropriate alcohol in the presence of a weak base.
- ✓ If a compound contains both hydroxy- and carboxylic acid groups, then cyclic esters or **lactones** can form via an intramolecular reaction. Reactions that form 5- or 6-membered rings are particularly favorable.



### Mechanism for Reaction for Acid Catalyzed Esterification

#### Step 1:

The O-atom of carbonyl groups accepts a proton. The protonation of the carbonyl makes it electrophilic. It is an acid/base reaction.

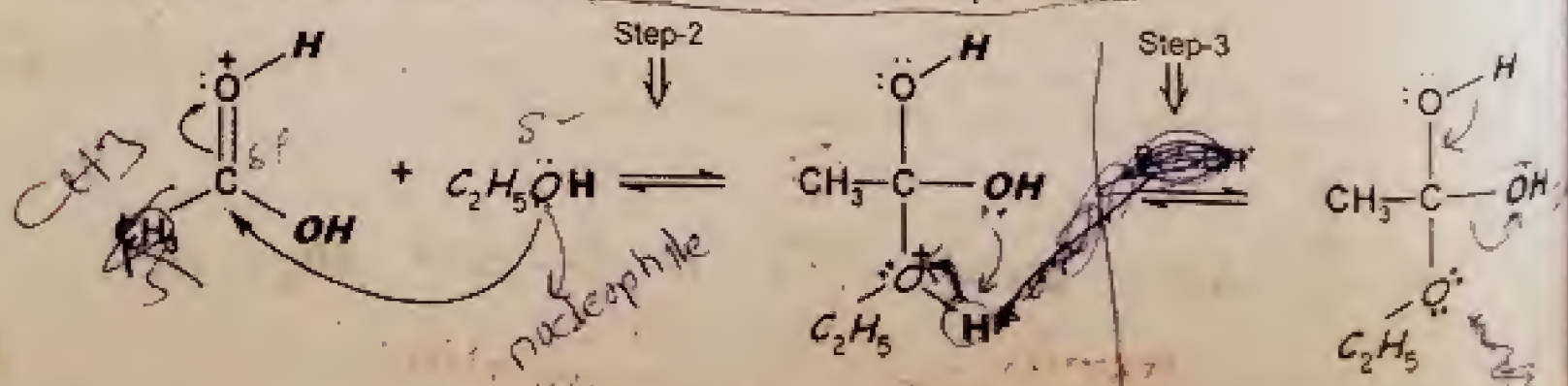


#### Step 2:

The O-atom of alcohol functions as the nucleophile and attacks the electrophilic C in the  $\text{C}=\text{O}$ . The electrons are moved towards the oxonium ion and a tetrahedral intermediate is formed.

#### Step 3:

An acid/base reaction occurs. The alcoholic oxygen atom is deprotonated.

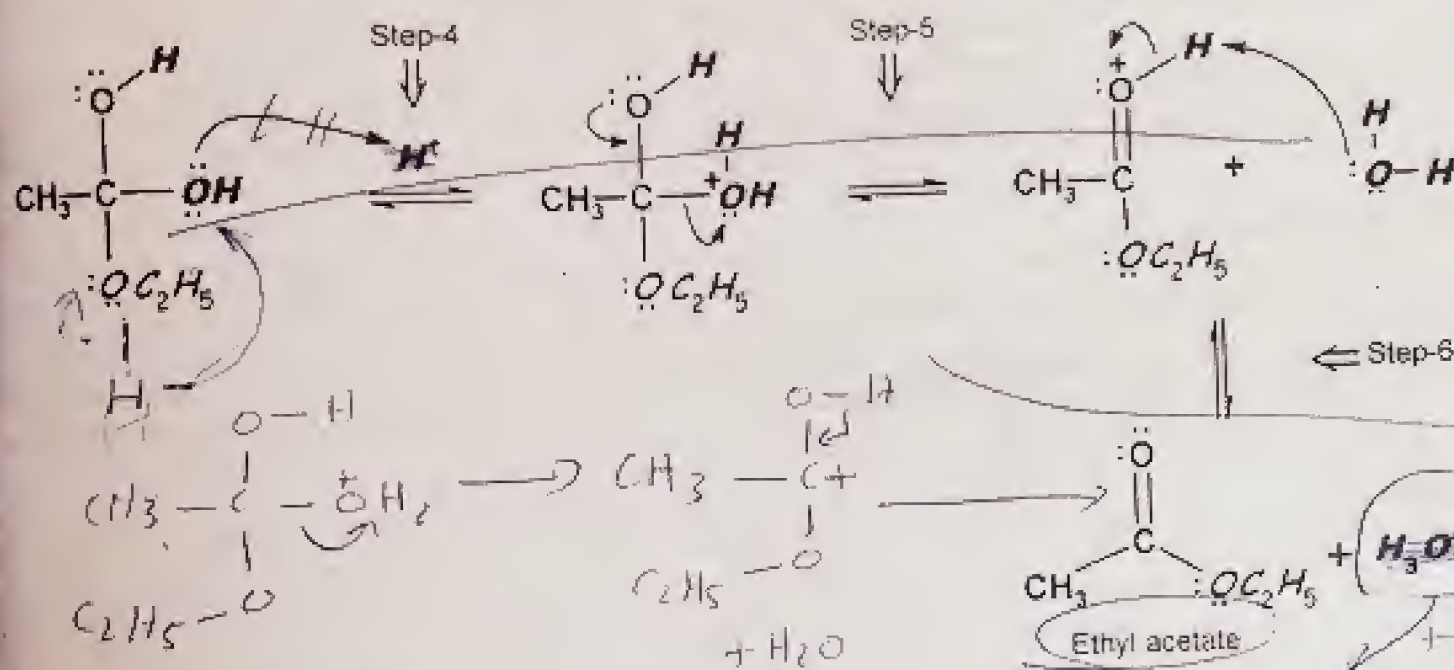




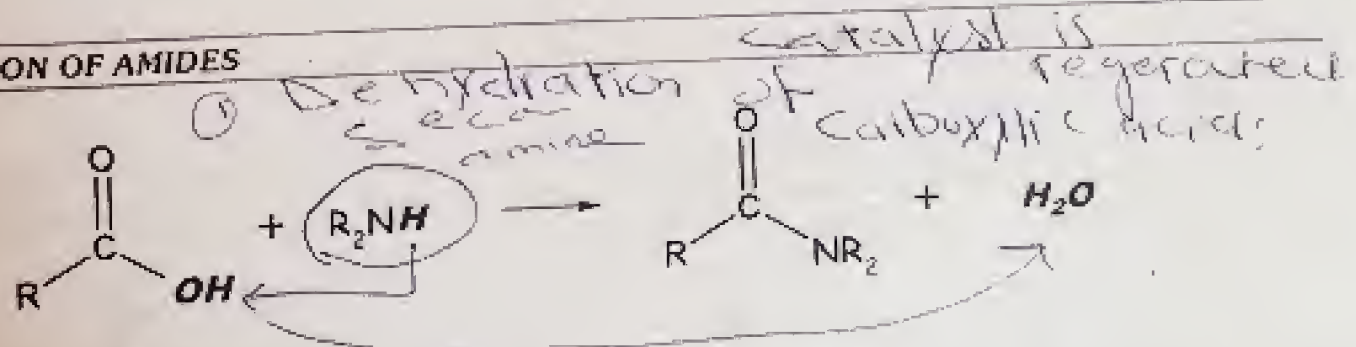
**Step 4:** An acid/base reaction occurs. The -OH is to be removed. However, it is not a good leaving group, therefore, it is converted into a good leaving group by protonation.

**Step 5:** The electrons of an adjacent oxygen help to "push out" the leaving group as a neutral water molecule. So, an oxonium ion is produced.

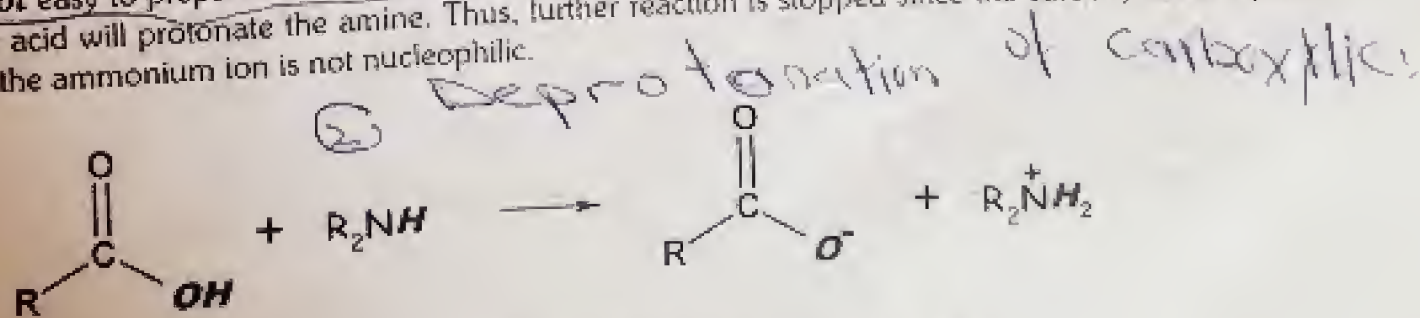
**Step 6:** An acid/base reaction occurs. The oxonium ion is deprotonated to give the ester product.



#### (4) PREPARATION OF AMIDES



In general, it is **not** easy to prepare amides directly from the parent carboxylic acid. It is because, the acid will protonate the amine. Thus, further reaction is stopped since the carboxylate is a poor electrophile and the ammonium ion is not nucleophilic.



It is much easier to convert the carboxylic acid to the more reactive acyl chloride first.



### (C) REACTION INVOLVING COOH GROUP AS A WHOLE

#### (1) REDUCTION TO ALCOHOLS

Carboxylic acids are reduced to **primary** alcohols.



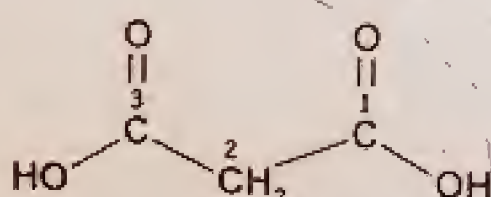
Carboxylic acids are less reactive to reduction by hydride than aldehydes, ketones or esters. Thus, carboxylic acids can only be reduced by  $\text{LiAlH}_4$  and **NOT** by the less reactive  $\text{NaBH}_4$ .

#### (2) DECARBOXYLATION

Loss of carbon dioxide is called **decarboxylation**.



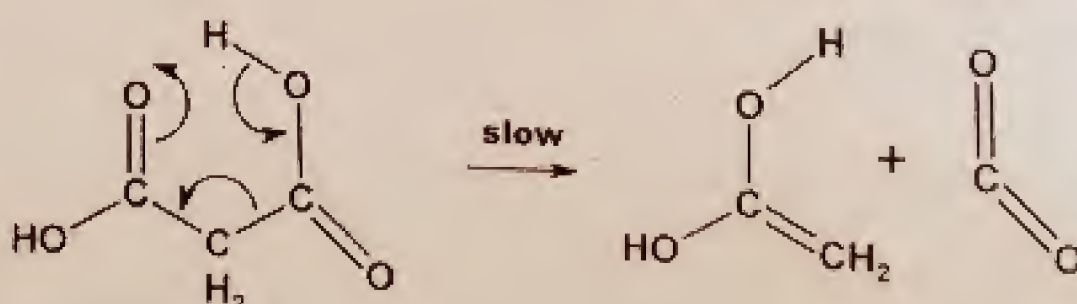
- Simple carboxylic acids rarely undergo decarboxylation.
- Carboxylic acids with a carbonyl group at the 3- (or  $\beta$ -) position readily undergo thermal decarboxylation e.g. derivatives of malonic acid.



The reaction proceeds via a cyclic transition state giving an enol intermediate that tautomerizes to the carbonyl product.

##### Step 1:

The reaction mechanism involves transfer of the proton from the O-H group of one COOH to the carbonyl oxygen of the other COOH group. Thus, O-H and C-C bonds are broken and  $\pi$ -bonds are formed. The reaction is a concerted nature.



##### Step 2:

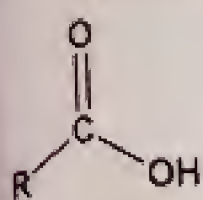
Tautomerization of the enol of the carboxylic acid forms the acid product.



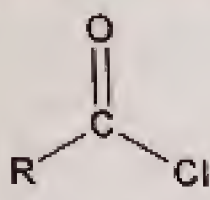


**ELABORATION OF REACTIONS THAT INTERCONVERT CARBOXYLIC ACIDS**

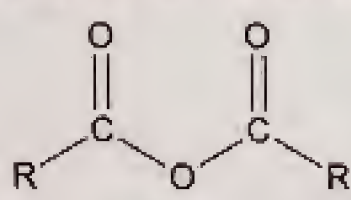
The carboxylic acid derivatives are a **family** of closely related functional groups:



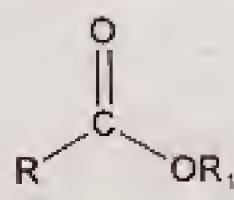
Carboxylic acid



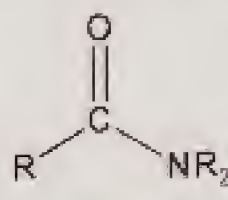
Acyl halide



Acid anhydride



Ester



Amide

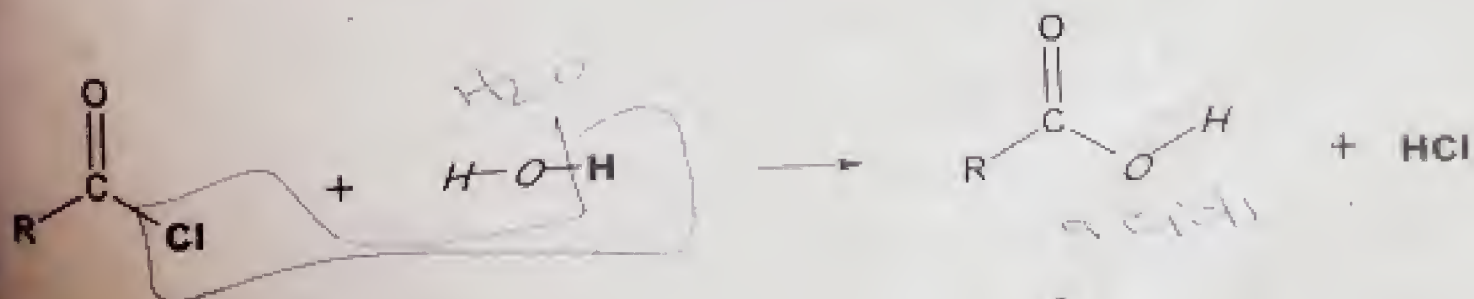
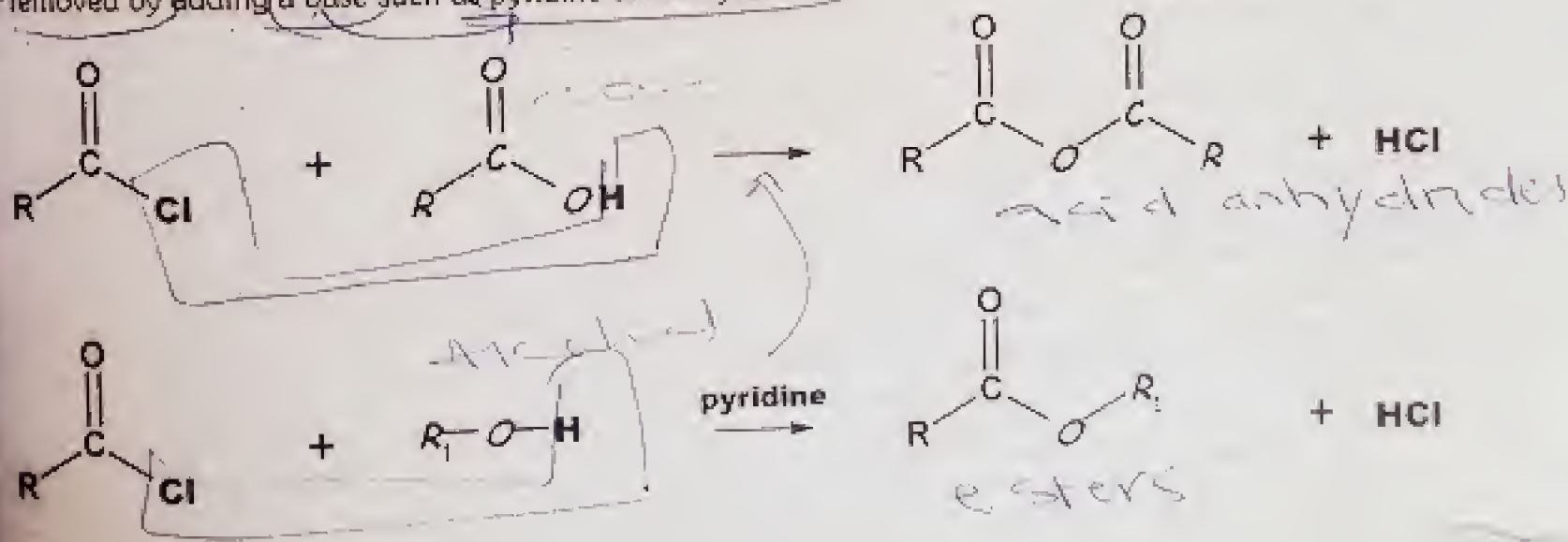
- Each contain a **C=O** group with a **heteroatom** attached. Thus, these are different from aldehydes and ketones.
- They can all be prepared from the "parent" carboxylic acid. On hydrolysis they all convert back to the parent carboxylic acid.
- They share a common reactivity pathway with nucleophiles called **Nucleophilic Acyl Substitution**.

**IMPORTANT**

The reactivity order is acyl chloride > anhydride > ester = carboxylic acid > amide > carboxylate

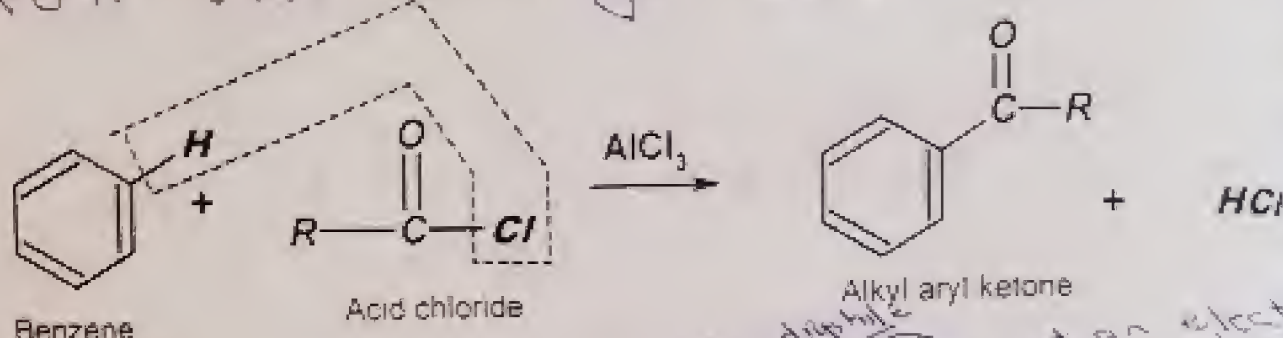
**REACTIONS OF CARBOXYLIC ACID DERIVATIVES****REACTIONS OF ACYL HALIDES**

- Acyl chlorides are the most reactive of the carboxylic acid derivatives. Therefore can be readily converted into other carboxylic acid derivatives.
- They react quite readily with cold water and hydrolyze to the carboxylic acid. The HCl by-product is usually removed by adding a base such as pyridine or triethyl amine.





# FRIEDEL-CRAFTS ACYLATION OF BENZENE



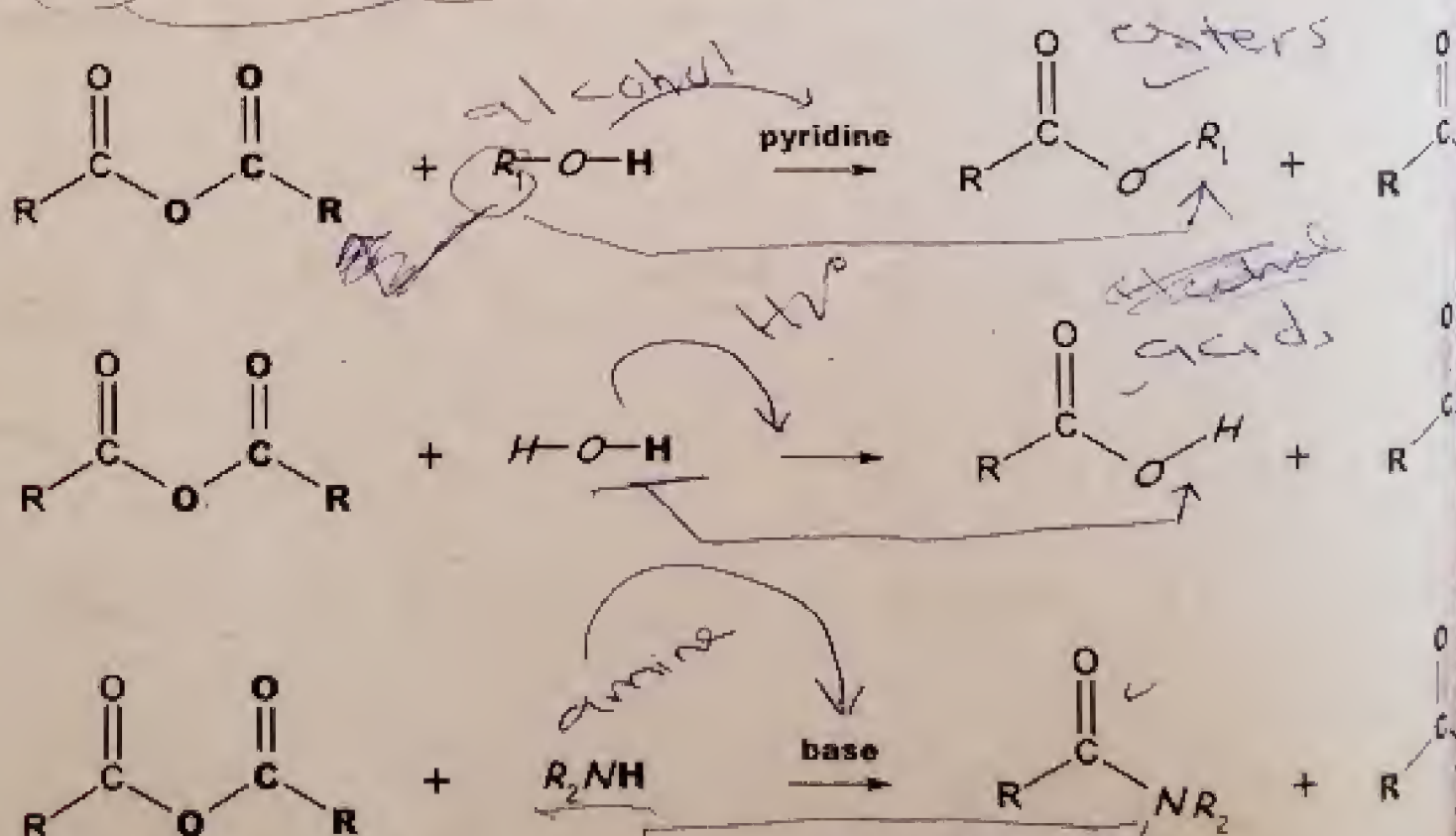
- Overall transformation: **Ar-H to Ar-COR** (a ketone)
- Named after Friedel and Crafts who discovered the reaction.
- Reagent:** normally the **acyl halide** (e.g. usually  $\text{RCOCl}$ ) with **aluminum trichloride,  $\text{AlCl}_3$** , a Lewis catalyst. *no rich in electron*
- The  $\text{AlCl}_3$  enhances the electrophilicity of the **acyl halide** by complexing with the halide. *electrophile accept an electron pair from a donor compound*
- Electrophilic species:** the acyl cation or **acylium ion** (i.e.  $\text{RCO}^+$ ) formed by the "removal" of the halide by the Lewis acid catalyst.
- Friedel-Crafts reactions are limited to arenes as or more reactive than **mono-halobenzenes**.
- Other sources of acylium can also be used such as acid anhydrides with  $\text{AlCl}_3$ .
- The reaction can still be called as a **Nucleophilic Acyl Substitution** of the acyl halide.

It is because overall we have a nucleophile (here the p-bond of an aromatic ring) replaces the leaving group (chloride) at the electrophilic  $\text{C=O}$ .

## REACTIONS OF ACID ANHYDRIDES

Acid anhydrides are the second most reactive of the carboxylic acid derivatives and can therefore be readily converted into the other less reactive carboxylic acid derivatives (see above).

- A base is often added to neutralize the carboxylic acid by product that is formed.



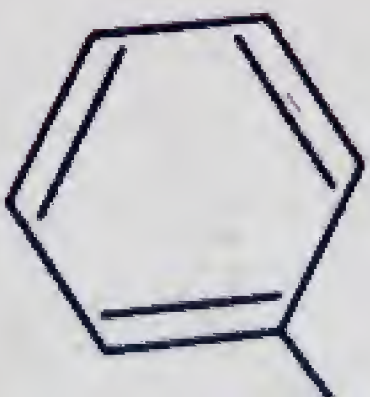
Lone pairs on amine base:  $\text{NH}_3, \text{H}_2\text{O}$   
Nucleophiles:  $\text{CH}_3\text{-S}^-$

Lewis acids:  
• Lone pairs accept  $\text{BF}_3, \text{AlCl}_3$   
• electrophile  $\text{Al}^{3+}, \text{Fe}^{3+}$   
• The proton



$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{R}' \end{array}$   
 A carbonyl group is a functional group with the formula  $\text{R}-\text{C}(=\text{O})-\text{R}'$  where  $\text{R}$  is bonded to the carbonyl carbon atom with a single bond. Carbonyl groups are formed from an oxoacid. In acids or more hydroxyl groups ( $-\text{OH}$ ) are removed from an oxoacid.

Ester / Ketones / aldehydes / amides  
 $\text{O}=\text{C}-\text{O}-\text{R}$  or  $\text{O}=\text{C}-\text{R}$   
 In these, the carbonyl carbon is bonded to an oxygen atom, which is bonded to another atom, with the exception of ketones where the carbonyl carbon is bonded to two other atoms.



Alkyl and

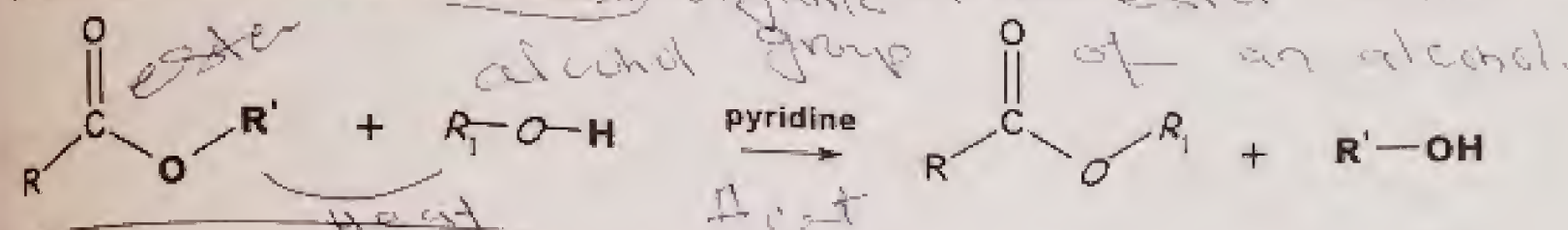
a functional group whose  
 bond is  
 a single bond.



## REACTIONS OF ESTERS

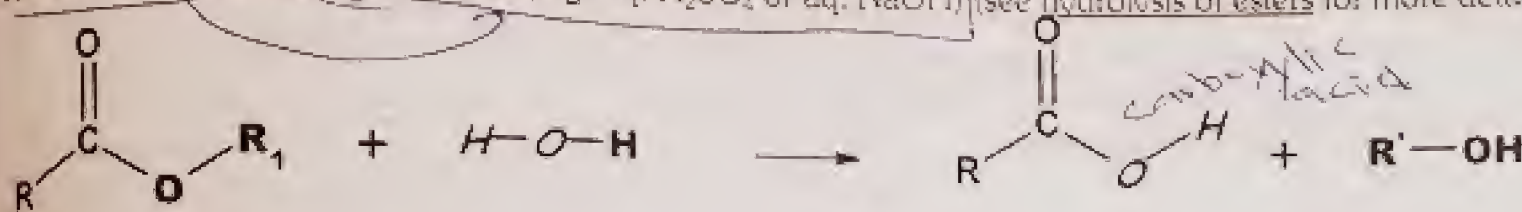
Esters can be converted into other esters (transesterification), the parent carboxylic acid (hydrolysis) or amides.

**TRANSESTERIFICATION:** is the process of exchanging the organic group of an ester with an alcohol group.



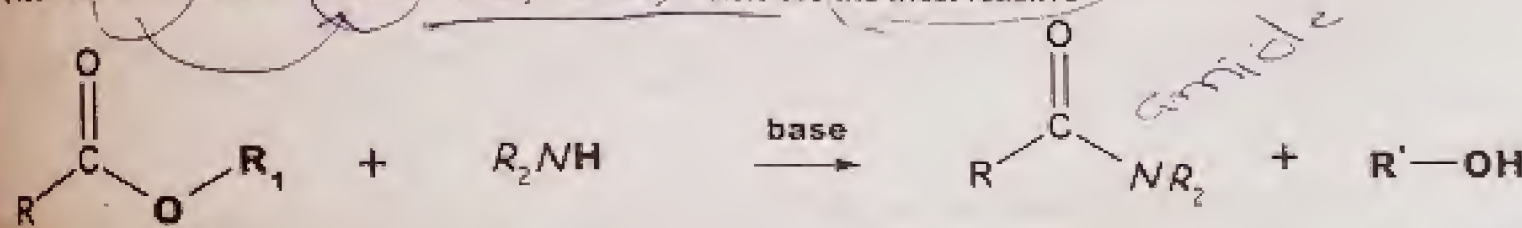
## HYDROLYSIS

Heat the ester with aq. acid or base (e.g. aq.  $\text{H}_2\text{SO}_4$  or aq.  $\text{NaOH}$ ) (see hydrolysis of esters for more details)



## AMIDE PREPARATION:

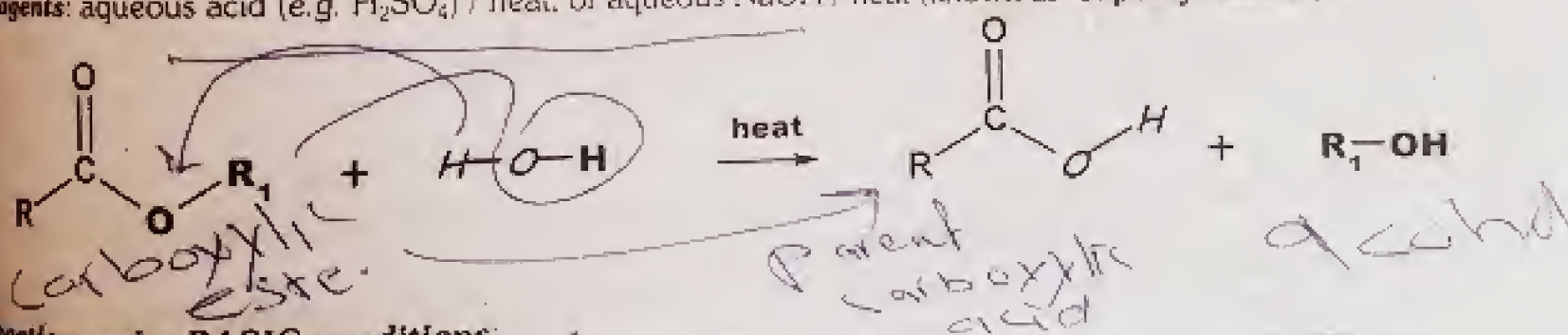
Heat the ester with the amine, methyl or ethyl esters are the most reactive



## HYDROLYSIS OF ESTERS

Carboxylic esters hydrolyze to the parent carboxylic acid and an alcohol.

Reagents: aqueous acid (e.g.  $\text{H}_2\text{SO}_4$ ) / heat. or aqueous  $\text{NaOH}$  / heat (known as "saponification").

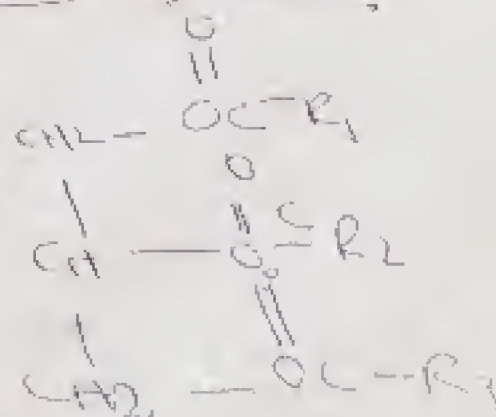


### Reaction under BASIC conditions:

- The mechanism shown leads to acyl-oxygen cleavage.
- The mechanism is supported by experiments using  $^{18}\text{O}$  labeled compounds and esters of chiral alcohols.
- This reaction is known as "saponification" because it is the basis of making soap from glycerol triesters in labs.
- The mechanism is an example of the reactive system type.

### Reaction under ACIDIC conditions:

- The acid catalyzed mechanism is the reverse of the Fischer esterification.
- The mechanism shown also leads to acyl-oxygen cleavage.
- The mechanism is an example of the less reactive system type.





## REDUCTION OF ESTERS

Carboxylic esters are reduced give 2 alcohols, one from the alcohol portion of the ester and a 1° alcohol from the reduction of the carboxylate portion.



- ✓ Esters are less reactive towards Nu than aldehydes or ketones.
- ✓ They can only be reduced by  $\text{LiAlH}_4$  and NOT by the less reactive  $\text{NaBH}_4$ .
- ✓ The reaction requires that 2 hydrides (H) be added to the carbonyl group of the ester.
- ✓ The mechanism is an example of the reactive system type.
- ✓ Note the aldehyde intermediate.

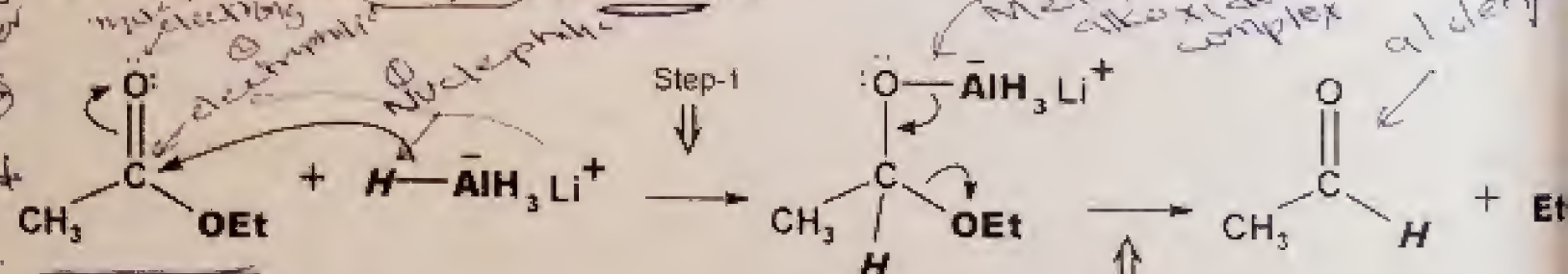
Binary compound of hydrogen with metal

### Step 1:

- The nucleophilic H from the hydride reagent adds to the electrophilic C in the polar carbonyl group of the ester.
- The electrons from the  $\text{C}=\text{O}$  move to the electronegative O creating an intermediate metal alkoxide complex.

### Step 2:

- The tetrahedral intermediate collapses and displaces the alcohol portion of the ester as a leaving group.
- This produces an aldehyde as an intermediate.

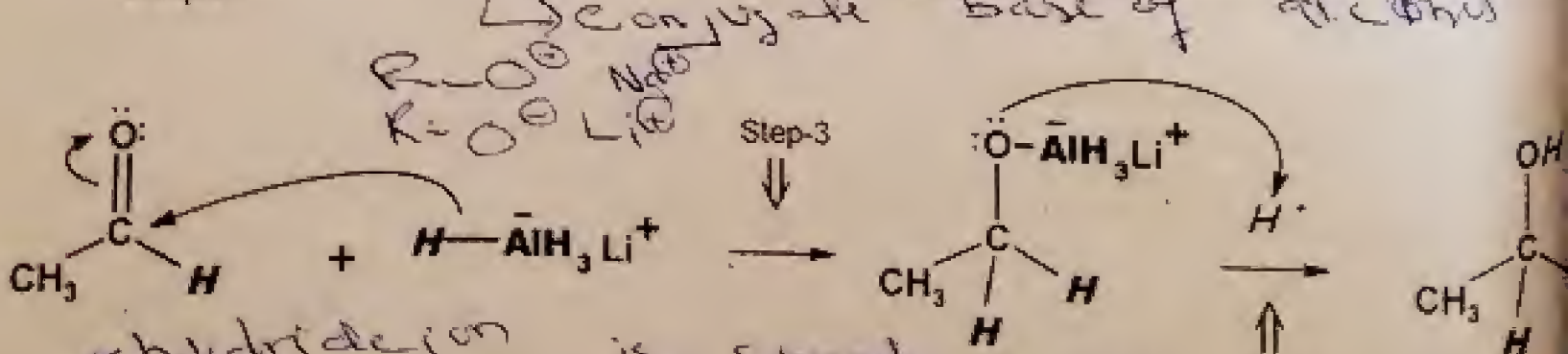


### Step 3:

- Now the aldehyde is reduced. The nucleophilic H from the hydride reagent adds to the electrophilic C in the polar carbonyl group of the aldehyde.
- The electrons from the  $\text{C}=\text{O}$  move to the electronegative O creating an intermediate metal alkoxide complex.

### Step 4:

- This is the work-up step. It is a simple acid/base reaction.
- Protonation of the alkoxide oxygen produces the primary alcohol product from the intermediate.

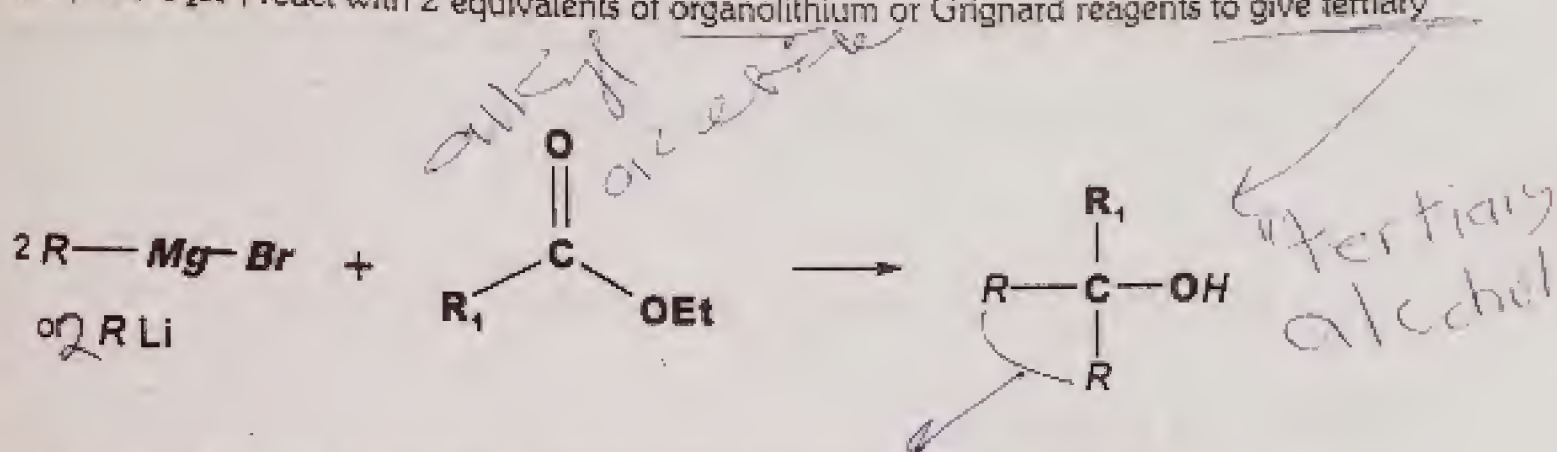


\*hydride ion is strongly basic but not nucleophilic. A reagent that acts as the hydride ion would if it were nucleophilic is called a hydride reagent.



**REACTIONS OF  $RLi$  AND  $RMgX$  WITH ESTERS**

Carboxylic esters,  $R'CO_2R''$ , react with 2 equivalents of organolithium or Grignard reagents to give tertiary alcohols.



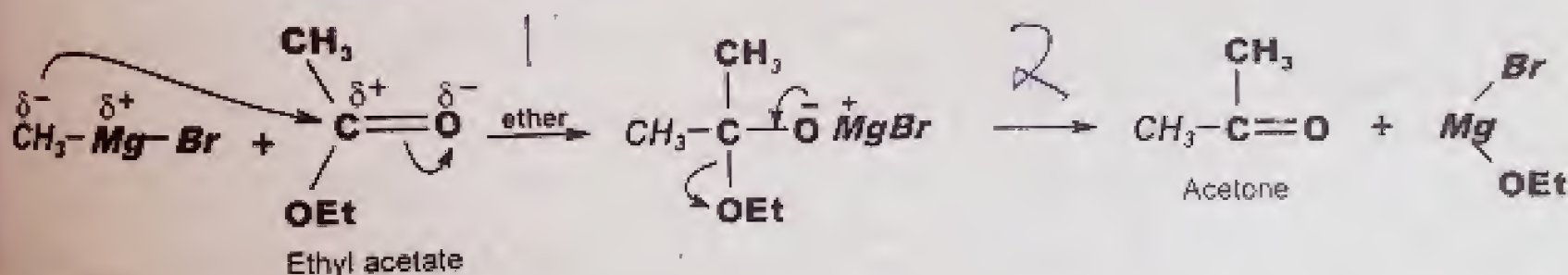
- ✓ The tertiary alcohol that results contains 2 identical alkyl groups (from  $R$  in the scheme)
- The reaction proceeds via a ketone intermediate which then reacts with the second equivalent of the organometallic reagent (review)
- ✓ Since the ketone is more reactive than the ester, the reaction cannot be used as a preparation of ketones.
- ✓ The mechanism is an example of the reactive system type.

**Mechanism****Step 1:**

- The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar carbonyl group of the ester.
- The electrons from the  $C=O$  move to the electronegative O creating an intermediate metal alkoxide complex.

**Step 2:**

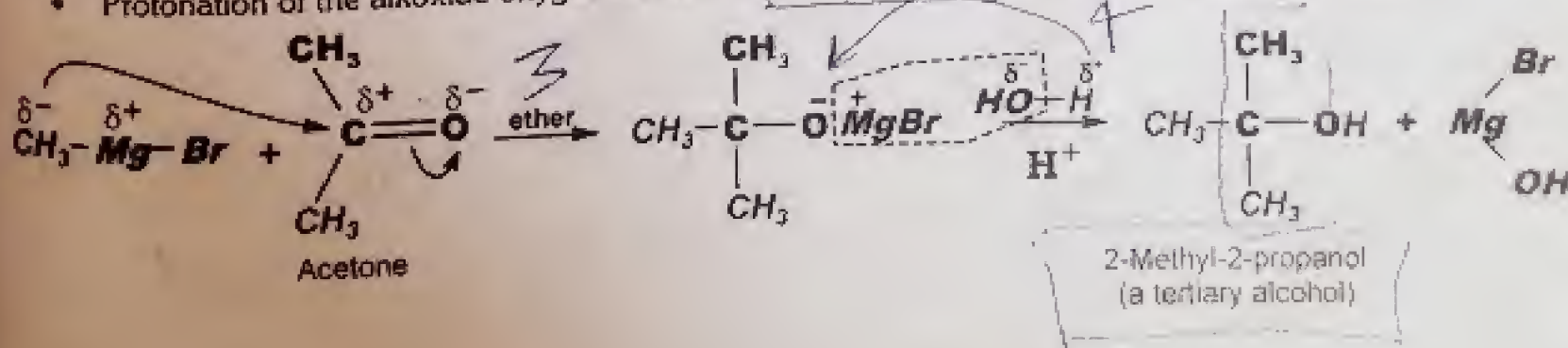
- The tetrahedral intermediate collapses and displaces the alcohol portion of the ester as a leaving group.
- This produces a ketone as an intermediate.

**Step 3:**

- The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar carbonyl group of the ketone.
- The electrons from the  $C=O$  move to the electronegative O creating an intermediate metal alkoxide complex.

**Step 4:**

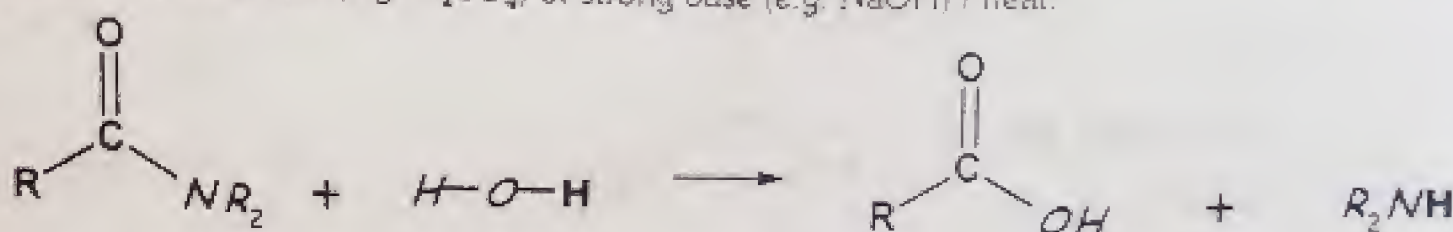
- This is the work-up step. It is a simple acid/base reaction.
- Protonation of the alkoxide oxygen creates the alcohol product from the intermediate complex.





## REACTIONS OF AMIDES

- Amides are the least reactive of the neutral carboxylic acid derivatives.
- The only interconversion reaction that amides undergo is hydrolysis back to the parent carboxylic acid and the amine.
- Reagents: Strong acid (e.g.  $\text{H}_2\text{SO}_4$ ) or strong base (e.g.  $\text{NaOH}$ ) / heat.



## HYDROLYSIS OF AMIDES

- Amides hydrolyze to the parent carboxylic acid and the appropriate amine.
- The mechanisms are similar to those of esters.
- Reagents: Strong acid (e.g.  $\text{H}_2\text{SO}_4$ ) / heat (preferred) or strong base (e.g.  $\text{NaOH}$ ) / heat.



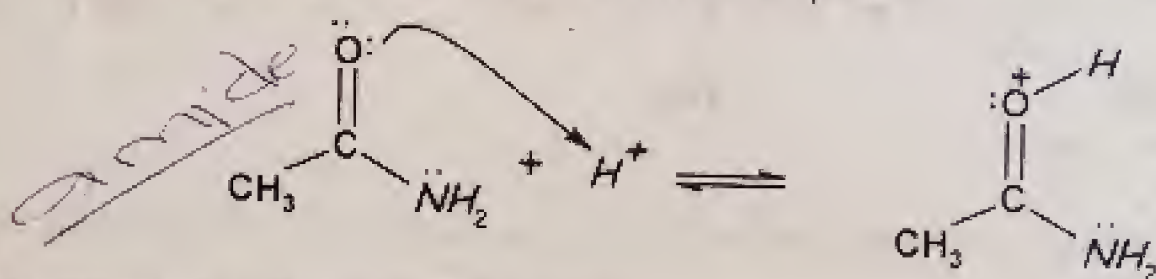
### REACTION UNDER ACIDIC CONDITIONS:

- Note that the acid catalyzed mechanism is analogous to the acid catalyzed hydrolysis of esters.
- The mechanism shown below proceeds via protonation of the carbonyl not the amide N (see step 1).
- The mechanism is an example of the less reactive system type.

### MECHANISM OF THE ACID CATALYZED HYDROLYSIS OF AMIDES

#### Step 1:

- It is an acid/base reaction.
- In this reaction water is a weak nucleophile and carbonyl group of amide is a weak electrophile. Thus the ester is first activated by protonation.
- Protonation of the amide carbonyl makes it more electrophilic.

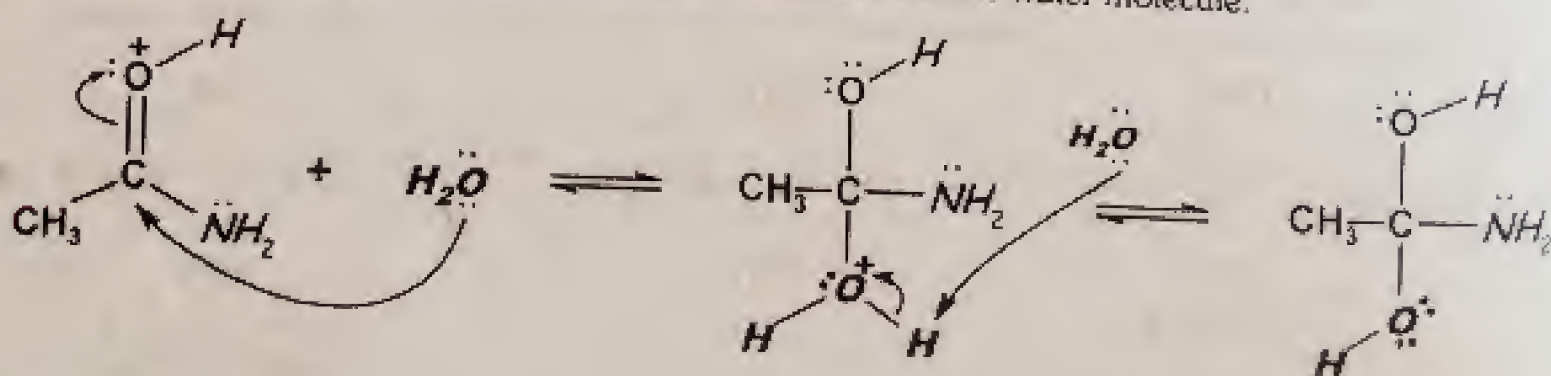


#### Step 2:

- The water O acts as the nucleophile and attacks the electrophilic C in the  $\text{C}=\text{O}$ .
- The electrons are moved towards the oxonium ion, creating the tetrahedral intermediate.

#### Step 3:

An acid/base reaction. Deprotonate the oxygen that came from the water molecule.





Step 4:

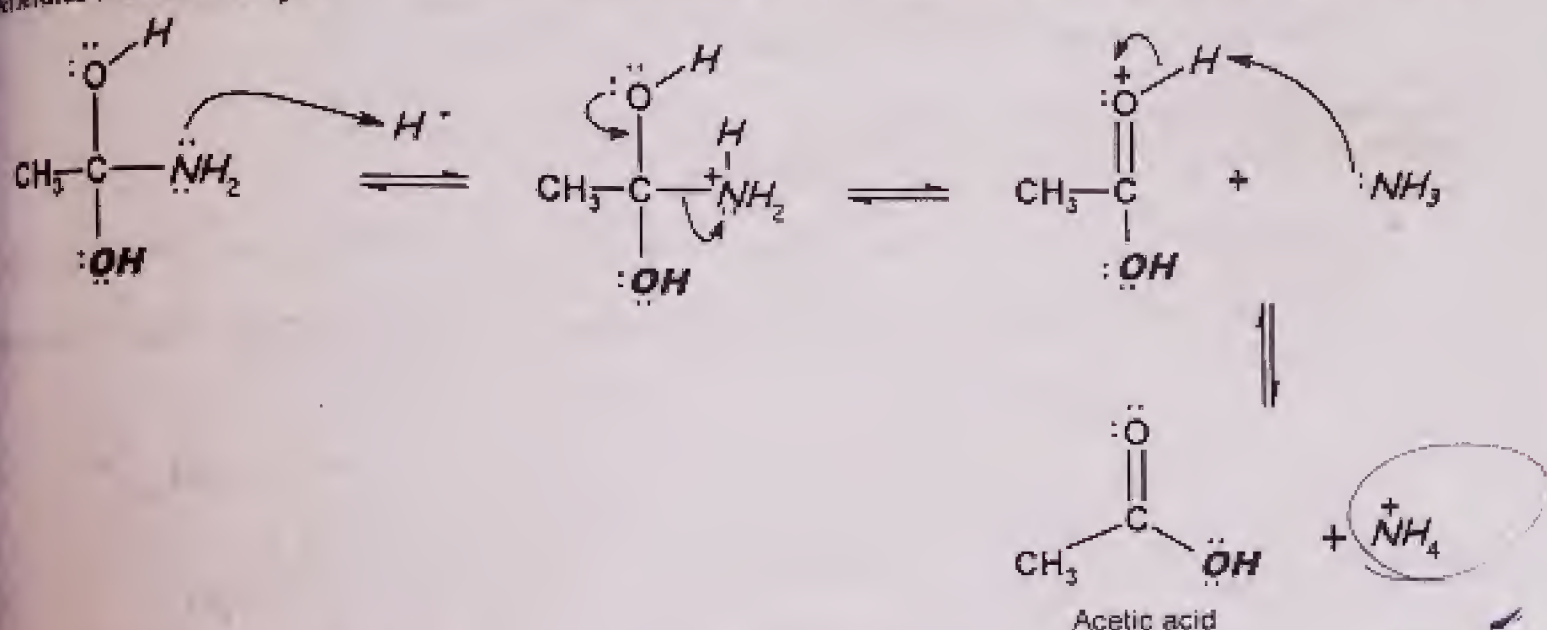
It is an acid/base reaction. The  $-NH_2$  group is to be removed. However, it is a poor leaving group. So, it is converted into a good leaving group by protonation.

Step 5:

The electrons of adjacent oxygen are used to help "push out" the leaving group as a neutral ammonia molecule. Thus, oxonium ion is produced.

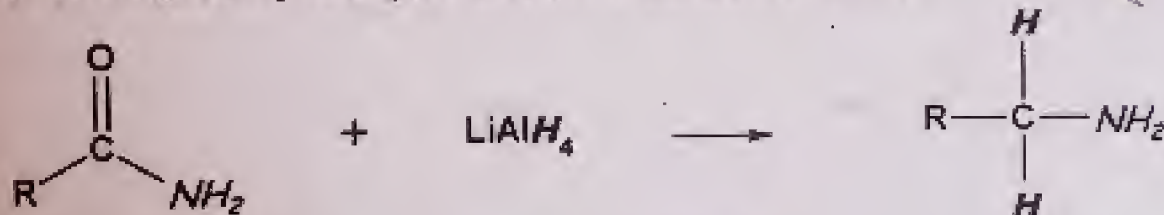
Step 6:

It is an acid/base reaction. Deprotonation of the oxonium ion forms the carboxylic acid product and regenerates the acid catalyst.



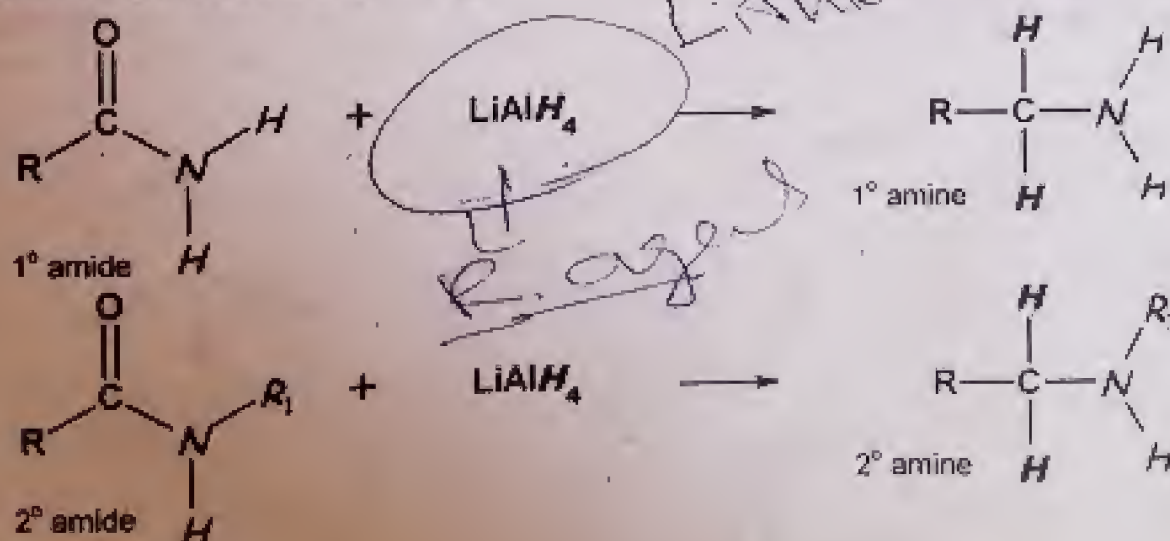
## REDUCTION OF AMIDES

- Amides,  $RCONR'_2$ , can be reduced to the amine,  $RCH_2NR'_2$  by conversion of the  $C=O$  to  $-CH_2-$ .
- Amides can be reduced by  $LiAlH_4$  but NOT by the less reactive  $NaBH_4$ .

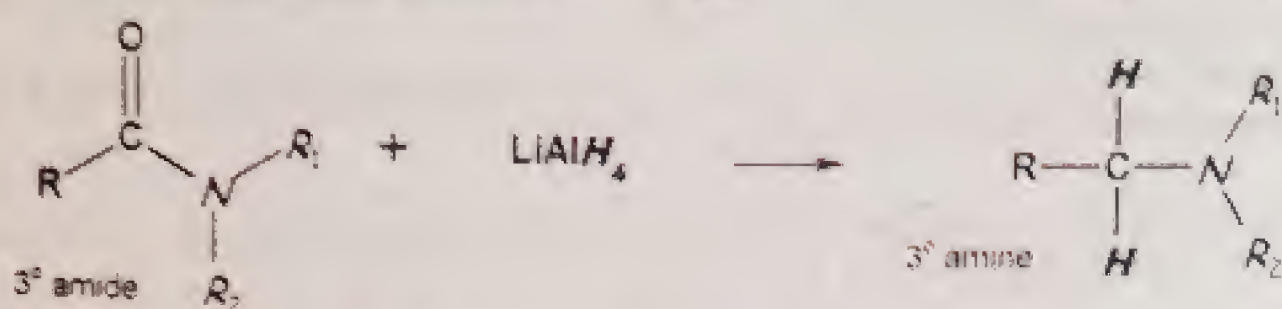


Typical reagents:  $LiAlH_4$  / ether solvent followed by aqueous work-up.

- This reaction is different to that of other  $C=O$  compounds which reduce to *alcohols*.
- The nature of the amine obtained depends on the substituents present on the original amide.
- The bonds to N substituents don't change.







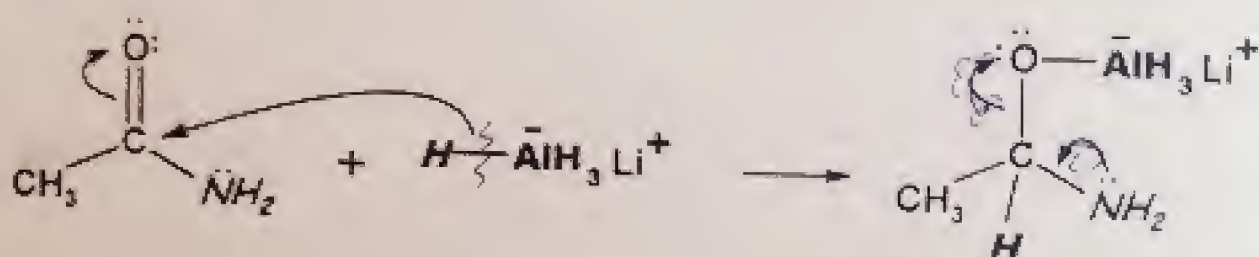
- R, R<sub>1</sub> or R<sub>2</sub> may be either alkyl or aryl substituents.
- In the potential mechanism note that it is an O system that leaves. This is because the O system better leaving groups than the less electronegative N systems.

**Exercise Q3 (III)** How amides are reduced with LiAlH<sub>4</sub>? Give mechanism.

**MECHANISM: REDUCTION OF AMIDE WITH LiAlH<sub>4</sub>**

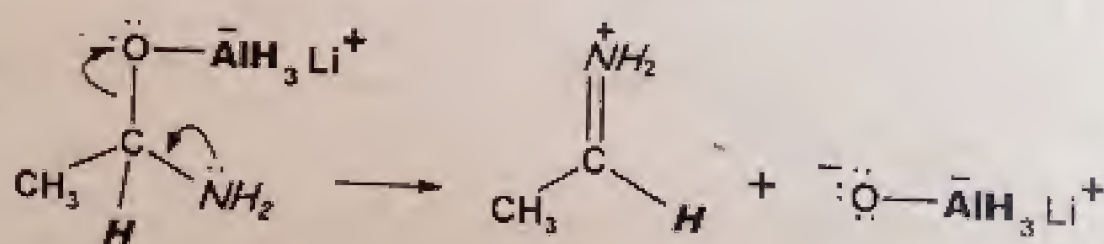
**Step 1:**

- The nucleophilic H from the hydride reagent adds to the electrophilic C in the polar carbonyl of the amide.
- The electrons from the C=O move to the electronegative O creating an intermediate metal alkoxide complex.



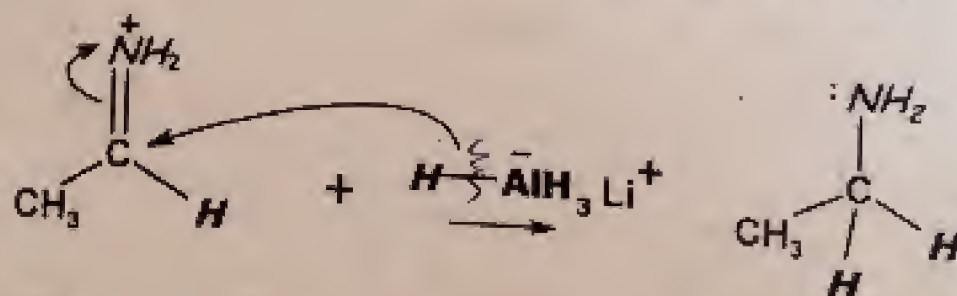
**Step 2:**

- The tetrahedral intermediate collapses and displaces the O as part of a metal alkoxide leaving group.
- This produces a highly reactive iminium ion intermediate.



**Step 3:**

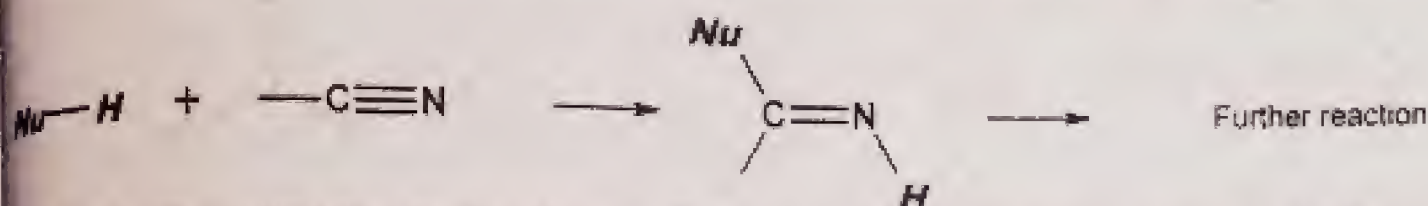
- The nucleophilic H from the hydride reagent adds to the electrophilic C in the iminium system.
- The π-electrons from the C=N move to the cationic N to neutralize the charge. Thus amine is produced.



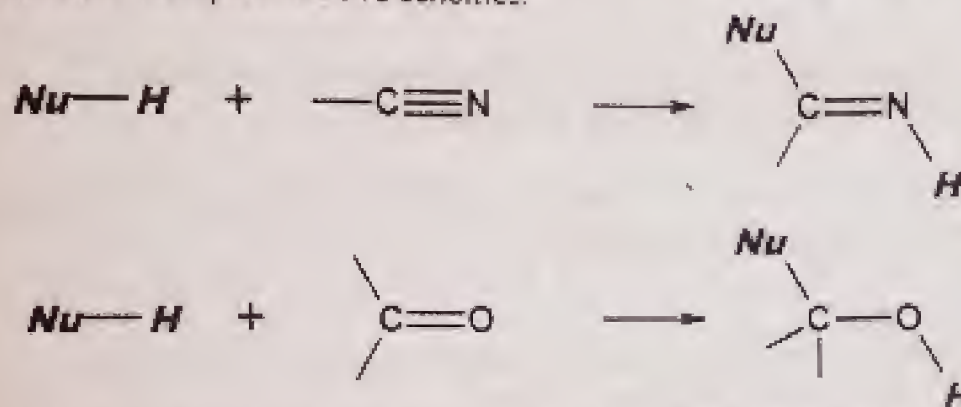


## REACTIONS OF NITRILES

Nitriles typically undergo nucleophilic addition to give products that often undergo a further reaction.



The chemistry of the nitrile functional group,  $\text{C}\equiv\text{N}$ , is very similar to that of the carbonyl,  $\text{C}=\text{O}$  of aldehydes and ketones. Compare the two schemes:

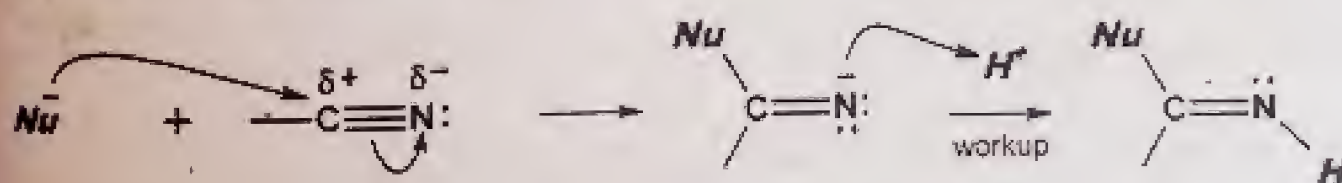


However, it is convenient to describe nitriles as carboxylic acid derivatives because:

- ✓ the oxidation state of the C is the same as that of the carboxylic acid derivatives.
- ✓ hydrolysis produces the carboxylic acid

Like the carbonyl containing compounds, nitriles react with nucleophiles in two ways:

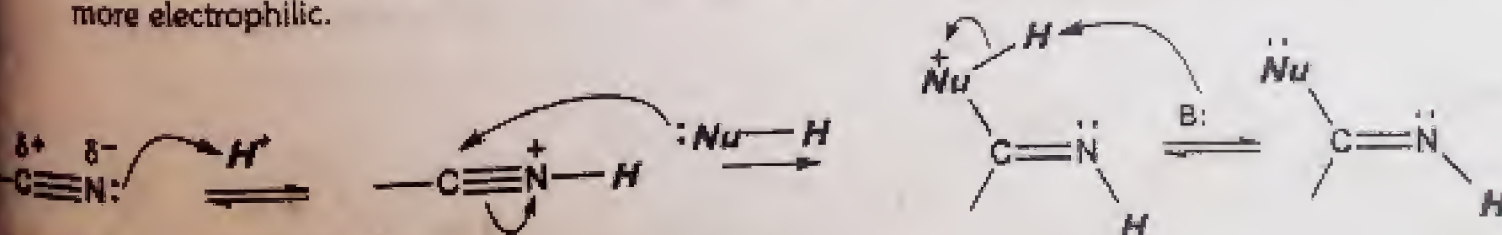
(1) **Strong nucleophiles** (anionic) add directly to the  $\text{C}\equiv\text{N}$  to form an intermediate imine salt that protonates (and often reacts further) on work-up with dilute acid.



Examples of such nucleophilic systems are:  $\text{RMgX}$ ,  $\text{RLi}$ ,  $\text{RC}\equiv\text{CM}$ ,  $\text{LiAlH}_4$

(2) **Weaker nucleophiles** (neutral) require that the  $\text{C}\equiv\text{N}$  be activated prior to attack of the Nu.

This can be done using an acid catalyst which protonates on the Lewis basic N and makes the system more electrophilic.



Examples of such nucleophilic systems are:  $\text{H}_2\text{O}$ ,  $\text{ROH}$

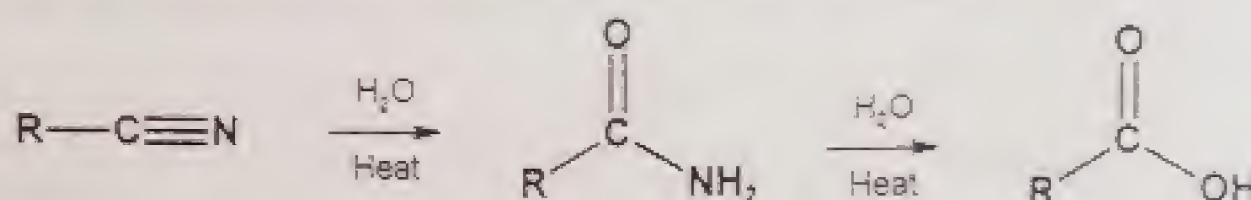
The protonation of a nitrile gives a structure that can be redrawn in another resonance form that reveals the electrophilic character of the C since it is a carbocation.





## HYDROLYSIS OF NITRILES

Nitriles,  $\text{RC}\equiv\text{N}$ , can be hydrolyzed to carboxylic acids,  $\text{RCO}_2\text{H}$  via the amide,  $\text{RCONH}_2$ .



**Reaction type:** Nucleophilic Addition then Nucleophilic Acyl Substitution

**Reagents:** Strong acid (e.g.  $\text{H}_2\text{SO}_4$ ) or strong base (e.g.  $\text{NaOH}$ ) / heat.

**Exercise Q2 (iv)** Give the mechanism for the acid catalyzed hydrolysis of a nitrile?

### MECHANISM: ACID CATALYZED HYDROLYSIS OF NITRILES

#### Step 1:

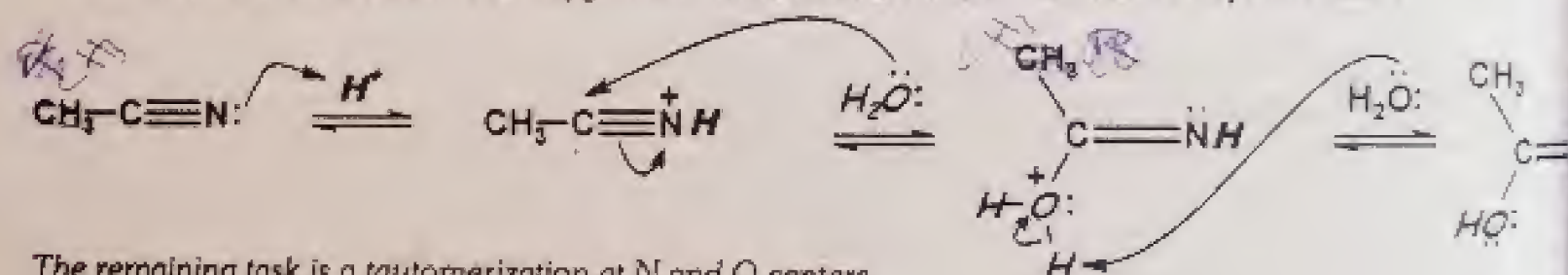
It is an acid/base reaction. Since, water is a weak nucleophile, therefore, the nitrile is first activated by protonation. So, the nitrile becomes more electrophilic.

#### Step 2:

- The water O acts as the nucleophile and attacks the electrophilic C in the  $\text{C}\equiv\text{N}$ .
- The electrons are moved towards the positive center.

#### Step 3:

It is an acid/base reaction. The oxygen that came from the water molecule is deprotonated



The remaining task is a tautomerization at N and O centers.

#### Step 4:

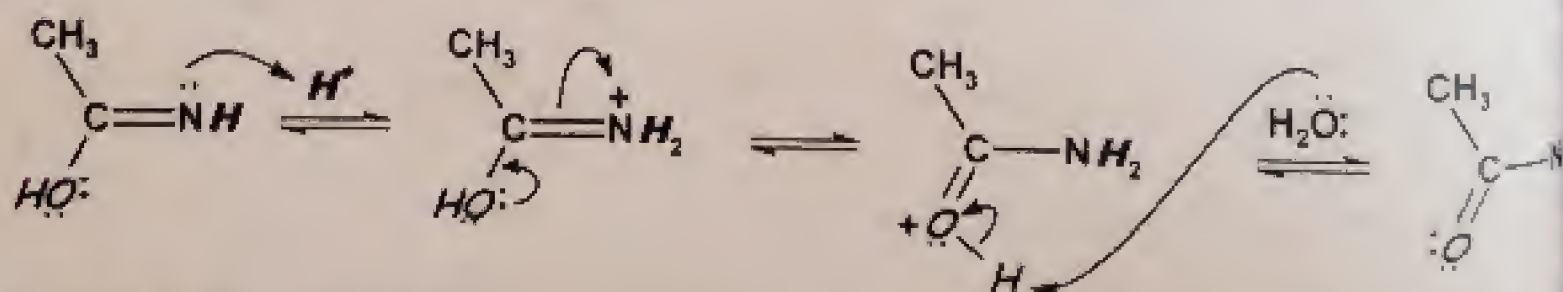
It is an acid/base reaction. The N atom is protonated to give the  $-\text{NH}_2$  group.

#### Step 5:

The electrons of an adjacent O are used to neutralise the positive charge at the N atom and a  $\text{C}=\text{O}$  bond is formed in the  $\text{C}=\text{O}$ . Thus, an oxonium is produced.

#### Step 6:

It is an acid/base reaction. The deprotonation of oxonium ion produces the amide intermediate.

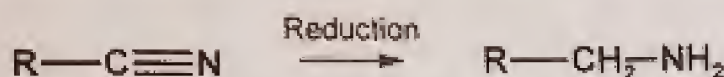


The amide intermediate is half-way to the formation of acid. The hydrolysis of amide occurs in the same way as described above in the "hydrolysis of amides"



## REDUCTION OF NITRILES

- The nitrile,  $\text{RC}\equiv\text{N}$ , gives the  $1^\circ$  amine by conversion of the  $\text{C}\equiv\text{N}$  to  $-\text{CH}_2\text{NH}_2$

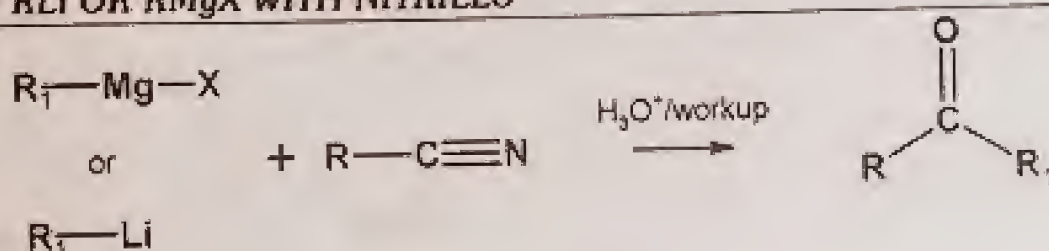


- Reactions usually in  $\text{Et}_2\text{O}$  or THF followed by  $\text{H}_3\text{O}^+$  work-up

Reaction type: Nucleophilic Addition

- Nitriles can be reduced by  $\text{LiAlH}_4$  but NOT the less reactive  $\text{NaBH}_4$ .
- Typical reagents:  $\text{LiAlH}_4$  / ether solvent followed by aqueous work-up.
- Catalytic hydrogenation ( $\text{H}_2$  / catalyst) can also be used giving the same products.
- R may be either alkyl or aryl substituents

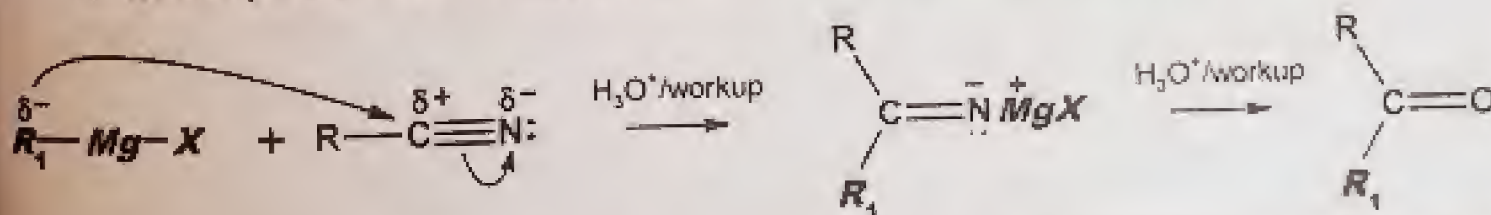
## REACTIONS OF $\text{RLi}$ OR $\text{RMgX}$ WITH NITRILES



Reaction usually occurs in  $\text{Et}_2\text{O}$  (Diethyl ether) or THF

Reaction type: Nucleophilic Acyl Substitution then Nucleophilic Addition

- Nitriles,  $\text{RC}\equiv\text{N}$ , react with Grignard reagents or organolithium reagents to give ketones.
- The strongly nucleophilic organometallic reagents add to the  $\text{C}\equiv\text{N}$  bond in a similar fashion to that seen for aldehydes and ketones.
- The reaction proceeds via an imine salt intermediate that is then hydrolyzed to give the ketone product.



- Since the ketone is not formed until **after** the addition of water, the organometallic reagent does not get the opportunity to react with the ketone product.
- Nitriles are less reactive than aldehydes and ketones.

## MECHANISM: REACTION OF $\text{RMgX}$ WITH AN NITRILE

Step 1:

- The nucleophilic C in the organometallic reagent adds to the electrophilic C in the polar nitrile group.
- The electrons from the  $\text{C}\equiv\text{N}$  move to the electronegative N creating an intermediate imine salt complex.

Step 2:

- It is an acid/base reaction.
- On addition of aqueous acid, the intermediate salt protonates giving the imine.

Step 3:

- It is an acid/base reaction.
- The imine is first activated by protonation (acid catalysis).



**Step 4:**

- The nucleophilic O of a water molecule attacks the electrophilic C in the imine.
- The  $\pi$ -electrons from the C=N move to the cationic N to neutralize the charge.

**Step 5:**

- It is an acid/base reaction.
- The O atom from the water molecule is deprotonated to neutralize the positive charge.

**Step 6:**

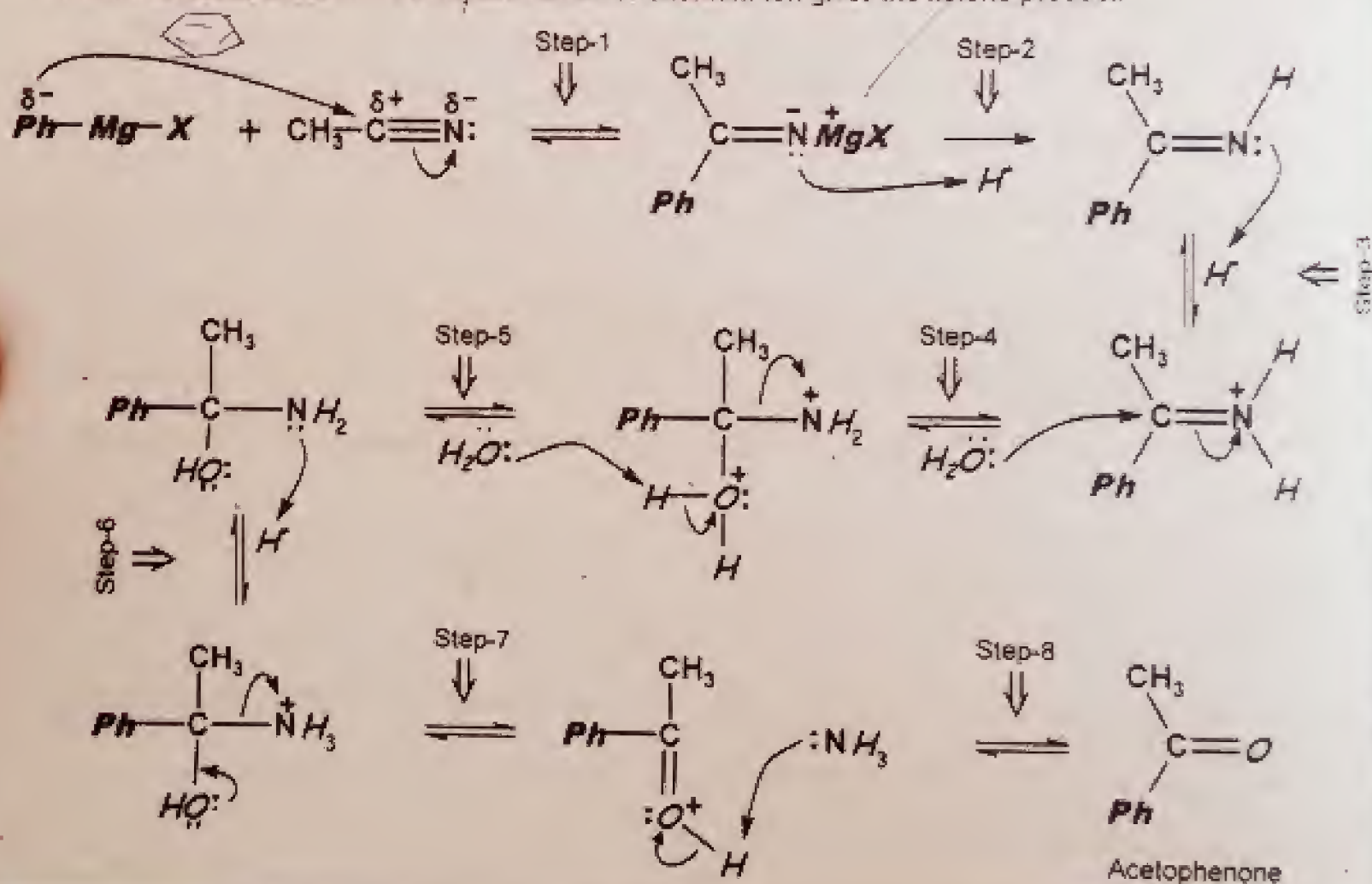
It is an acid/base reaction. The N system is converted into a better leaving group by protonation.

**Step 7:**

The electrons on the adjacent O are used to push out the N leaving group, as a neutral molecule of ammonia. An oxonium ion is produced.

**Step 8:**

It is an acid/base reaction. The deprotonation of oxonium ion gives the ketone product.



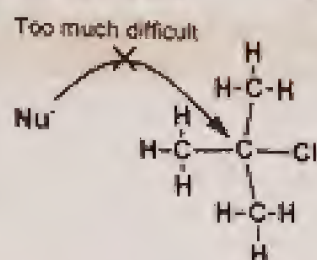
## QUICK QUIZ

**(1) Define Steric effect?**

The effect of the three-dimensional configuration of reacting substances on the rate, nature, and extent of reaction is called steric effect.

e.g. The steric effect of three methyl groups in ter-butyl chloride causes hindrance to the approach of nucleophile on tertiary carbon. Therefore, tertiary butyl chloride does not give  $\text{S}_\text{N}2$  reaction. Instead it gives  $\text{S}_\text{N}1$  reaction. This hindrance is called steric hindrance.





(2) What is alcohol's reactivity order?

- Alcohol reacts with other reagents due to the breaking of C-O and O-H bonds.
- If a nucleophile attacks, the C-O bonds break. The order of reactivity of alcohols with respect to cleavage of C-O bond is

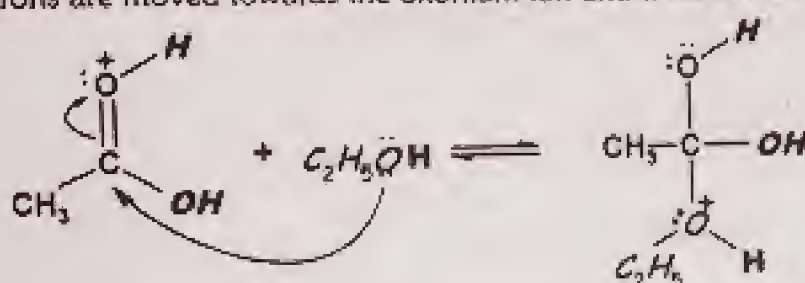
Tertiary alcohol > Secondary alcohol > Primary alcohol

- If an electrophile attacks the O-H bond breaks. The order of reactivity of alcohol with respect to O-H bonds cleavage:

$\text{CH}_3\text{OH} > \text{Tertiary alcohol} > \text{Secondary alcohol} > \text{Primary alcohol}$

(3) How oxonium ion creates the tetrahedral intermediate

- The O-atom of alcohol functions as the nucleophile and attacks the electrophilic C in protonated carbonyl compound.
- The electrons are moved towards the oxonium ion and a tetrahedral intermediate is formed.



(4) Define tautomerization?

The process of conversion of one tautomer into the other is called tautomerization.

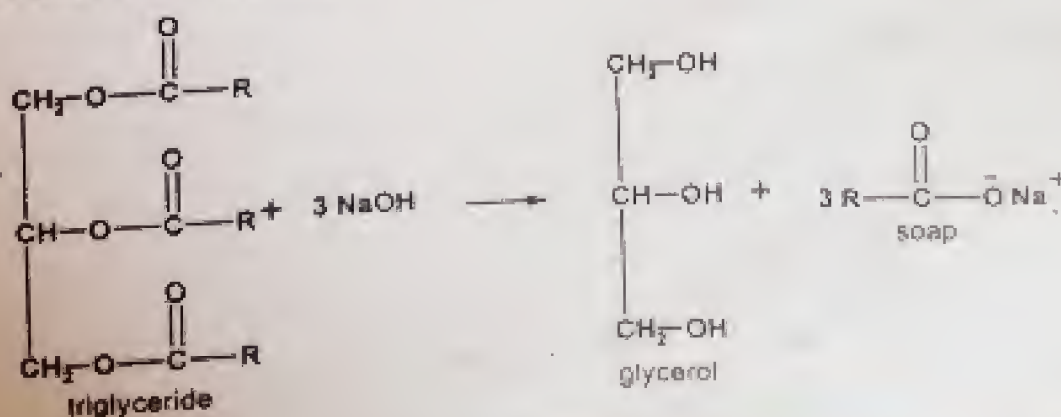


(5) Define saponification?

The hydrolysis of fats with alkalis to produce soap is called saponification reaction.

In this reaction sodium or potassium salt of fatty acids are produced. These salts are called soaps.

Glycerol is also produced as a by-product.





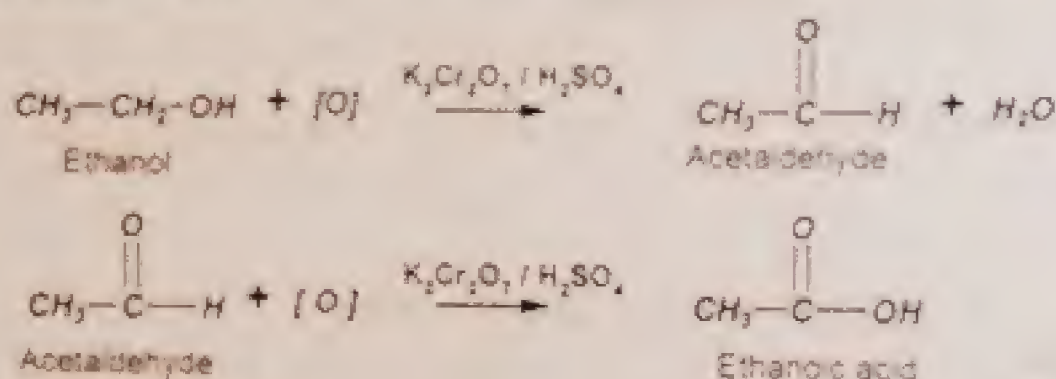
### DO YOU KNOW?

- (1) The carboxylic acid, 3-methyl-3-hexanoic acid is one of the compounds associated with the odor of human perspiration
- (2) The vinegaroon (whip-tail scorpion) expels a spray of acetic acid to repel predators
- (3) Flavour of some esters
 

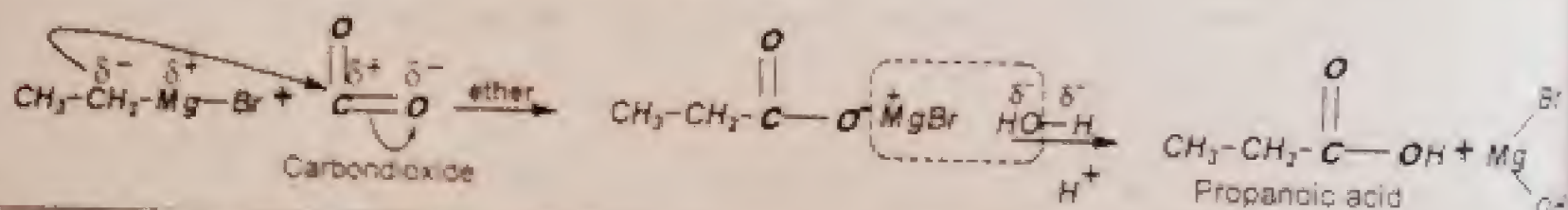
Amylacetate	Banana
Isobutyl formate	Raspberry
Benzyl acetate	Jasmine
Ethyl butyrate	Pineapple
Amyl butyrate	Apricot
Octyl Acetate	Orange
- (4) A peptide containing mass more than 10000 is known as protein.

### SOME IMPORTANT CONVERSIONS

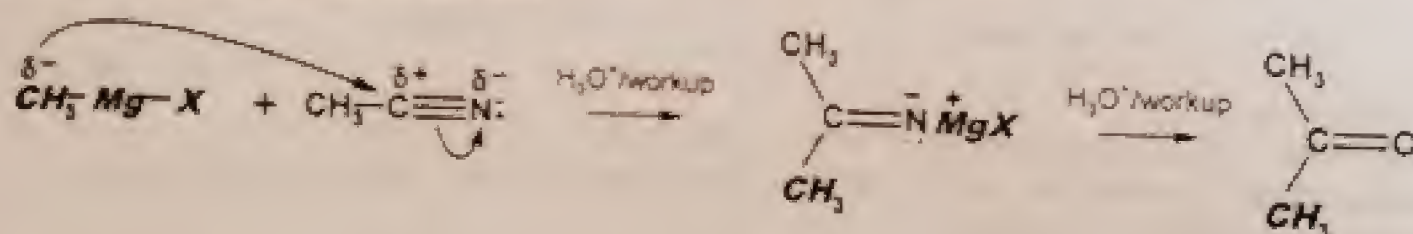
#### (i) Ethanol into ethanoic acid



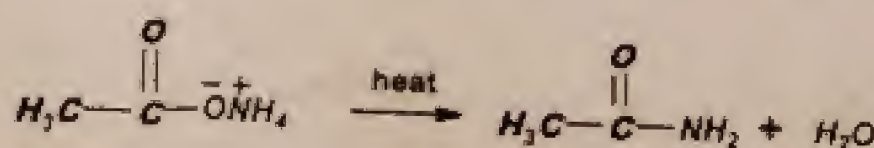
#### (ii) Ethyl bromide to propanoic acid



#### (iii) Ethyl magnesium bromide to acetone



#### (iii) Acetic acid to Acetamide





**SOCIETY, TECHNOLOGY AND SCIENCE****CARBOXYLIC ACIDS OCCURANCE.**

- Sorbic acid
- Caprylic acid is present in coconut
- Lauric acid is also present in coconut
- Myristic acid is present in nutmeg
- Arachidic acid is present in peanut oil
- Citric acid is present in citrus fruits e.g. lemon, limes, grapes, oranges.
- Tartaric acid is present in tamarind.
- Lactic acid is present in apples, tomatoes and molasses.
- Acetic acid is present in grapes.
- Malic acid is present in green apples and plums.
- Benzoic acid is found in berries.
- Butyric acid is present in rancid butter.
- Caproic acid is present in goat fat.
- Caprylic acid is present in milk.
- Palmitic acid is present in palm oil.
- Stearic acid is present in waxes, animal fats and oils.
- Amino acids are the building blocks of proteins.
- Acetoacetic acid and pyruvic acid are the acids of biochemical significance.
- Lactic acid is found in sour milk.
- Tartaric acid is found in wine.
- Acetic acid is found in vinegar.

**CARBOXYLIC ACIDS AS FOOD PRESERVATIVES.**

**Formic acid** is used as preservative for silage (including fresh hay) and other livestock feed.

**Boric acid** was used as a food preservative in caviar (a product made from salt-cured fish-eggs) but its use has been banned now.

**Salicylic acid** Its use has been banned now.

**Benzoic acid** is used as a preservative in jams, beer, preserved fruit, pickles, fruit juice, desert sauces and syrups.

**Acetic acid** is used as a preservative in fish fingers, butter, margarine, processed cheese, curry powder, cooking oil.

**Lactic acid** is used as a preservative in beer, tinned foods especially vegetables and fruit, fresh fruit and vegetables.

**Propionic acid** is used as a preservative in dairy products, particularly in cheese and in baking products.

**TASTE OF DIFFERENT CARBOXYLIC ACIDS.**

- Esters are derived from carboxylic acids by reaction of carboxylic acids and alcohols in the presence of hydrochloric acid or sulfuric acid, a process called esterification.
- Ester flavors are a range of fruity, sugary and sweet that occur in many beer types as a normal part of their brewing process.
- Examples of ester flavors are

**Ethyl formate** gives raspberries their characteristic taste.

**Ethyl acetate** has a bittersweet, wine-like burning taste.

**Isoamyl acetate** has a taste reminiscent of pears or bananas.

**Ethyl propionate** has rum like taste. (Rum is distilled alcoholic beverage made from sugarcane byproducts).

**Ethyl butyrate** -found in pineapples- tastes like sugar water.



**Ethyl valerate** has apple like taste.

**Ethyl hexanoate** is an apple-flavoured ester.

**Ethyl heptanoate** has wine-like odour and taste with a burning after-taste.

**Ethyl octanoate** found in pineapples has sweet taste.

### KEY POINTS

- Carboxylic acids are the most acidic of the common organic functional groups.
- The  $\text{CO}_2\text{H}$  unit is planar and consistent with  $\text{sp}^2$  hybridization and a resonance interaction of the lone pairs of the hydroxyl oxygen with the  $\pi$  system of the carbonyl.
- The most important reactions of carboxylic acids converts them into carboxylic acid derivatives such as acyl halides, esters and amides via nucleophilic acyl substitution reactions.
- Esters can also be made from other carboxylic acid derivatives, especially acyl halides and anhydrides, by reacting them with the appropriate alcohol in the presence of a weak base.
- Loss of carbon dioxide is called **decarboxylation**.
- Simple carboxylic acids rarely undergo decarboxylation
- Esters are less reactive towards  $\text{Nu}$  than aldehydes or ketones.
- Carboxylic esters,  $\text{R}_1\text{COOR}_2$ , react with 2 equivalents of organolithium or Grignard reagents to give tertiary alcohols.
- Amides hydrolyze to the parent carboxylic acid and the appropriate amine.
- Amides can be reduced by  $\text{LiAlH}_4$  but **NOT** the less reactive  $\text{NaBH}_4$ .
- The chemistry of the nitrile functional group,  $\text{C}\equiv\text{N}$ , is very similar to that of the carbonyl,  $\text{C}=\text{O}$  of aldehydes and ketones.
- Nitriles,  $\text{RC}\equiv\text{N}$ , react with Grignard reagents or organolithium reagents to give ketones.



## EXERCISE

**Q1: Select the right answer from the choices given with each question.**

- (i) A carboxyl acid contains functional group:
  - (a) A Hydroxyl group
  - (b) A Carboxyl group
  - (c) A Hydroxyl and Carboxyl group
  - (d) A Carboxyl and aldehyde group
- (ii) From the following carboxylic acids which acid has higher acidity:
  - (a) Ethanoic acid
  - (b) Propanoic acid
  - (c) Chloroethanoic acid
  - (d) Nitroethanoic acid
- (iii) Which reagent is used to reduce a carboxylic acid?
  - (a)  $\text{H}_2/\text{Ni}$
  - (b)  $\text{H}_2/\text{Pt}$
  - (c)  $\text{NaBH}_4$
  - (d)  $\text{LiAlH}_4$
- (iv) Stronger acid is
  - (a)  $\text{CH}_3\text{COOH}$
  - (b)  $\text{HCOOH}$
  - (c)  $\text{CH}_3\text{CH}_2\text{COOH}$
  - (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$
- (v) Acetamide is prepared by:
  - (a) Heating ammonium acetate
  - (b) Heating methyl cyanide
  - (c) Heating ethyl acetate
  - (d) The hydrolysis of methyl cyanide
- (vi) Carboxylic acids react with metal to form salts with the evolution of
  - (a)  $\text{CO}_2$
  - (b)  $\text{H}_2$
  - (c) CO
  - (d)  $\text{CH}_4$
- (vii) Ethane-1,2-dioic acid is also called:
  - (a) Benzoic acid
  - (b) Oxalic acid
  - (c) Formic acid
  - (d) Malonic acid
- (viii) Carboxylic acid can be prepared by the action of Grignard's reagent with
  - (a)  $\text{O}_2$
  - (b)  $\text{CO}_2$
  - (c) KCl
  - (d)  $\text{N}_2$
- (ix) The IUPAC name for formic acid is
  - (a) Methanoic acid
  - (b) Acetic acid
  - (c) Ethanoic acid
  - (d) Butanoic acid
- (x) The reaction of alcohol with acetic acid is known as
  - (a) saponification
  - (b) esterification
  - (c) ammonolysis
  - (d) hydrolysis
- (xi) Esters are formed by the reaction of carboxylic acids with
  - (a) alcohols
  - (b) ethers
  - (c) aldehydes
  - (d) Alkyl halides
- (xii) Which one of the following has both hydroxyl and carboxylic acid groups?
  - (a) phenol
  - (b) picric acid
  - (c) phthalic acid
  - (d) Salicylic acid
- (xiii) Which of the following cannot be prepared directly from acetic acid
  - (a) acetamide
  - (b) acetyl chloride
  - (c) acetic anhydride
  - (d) Ethyl acetate
- (xiv) Reaction between caustic soda and a fat is called
  - (a) esterification
  - (b) hydrogenation
  - (c) neutralization
  - (d) saponification
- (xv) When a carboxylic acid reacts with alcohol, it produces a new class of compounds.
  - (a) ethers
  - (b) esters
  - (c) anhydride
  - (d) amide

## ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (b) A Carboxyl group

A carboxylic acid contains a carboxyl group ( $\text{COOH}$ ).

(iii) Ans: (d)  $\text{LiAlH}_4$

$\text{LiAlH}_4$  reduces carboxylic acids to alcohols

(v) Ans: (a) Heating ammonium acetate



Ammonium acetate

Acetamide

(vii) Ans: (b) Oxalic acid

$\text{COOH}$

$\text{COOH}$  (Ethanedioic acid or Oxalic acid)

(ix) Ans: (a) Methanoic acid

Since Formic acid ( $\text{HCOOH}$ ) contains one carbon, so it is methanoic acid.

(ii) Ans: (d) Nitroethanoic acid

The nitro group is a strong electron withdrawing group, so it increases the acidity

(iv) Ans: (b)  $\text{HCOOH}$

Alkyl groups attached to  $\text{COOH}$  group decreases the acidity by their electron donating effect.

(vi) Ans: (b)  $\text{H}_2$



(viii) Ans: (b)  $\text{CO}_2$

Grignard's reagent react with  $\text{CO}_2$  to form an intermediate which on acid hydrolysis produces carboxylic acid.

(x) Ans: (b) esterification

The reaction of alcohol with acid is called esterification. So, this reaction is called esterification.

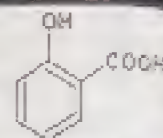


**(xi) Ans: (a) alcohols**

The reaction of carboxylic acid with alcohol produces an ester. This reaction is called esterification reaction.

**(xii) Ans: (d) Salicylic acid**

The formula of Salicylic acid shows that it contains both hydroxyl group (OH) and carboxyl group (COOH).



**(xiii) Ans: (a) acetamide**

Since reaction of acetic acid with ammonia first produce ammonium acetate. It is then heated to give acetamide.

[See also MCQ no. (v)]

**(xiv) Ans: (d) saponification**

The reaction of fat with caustic soda produces soap. So, this reaction is called saponification reaction.

[Also see CH#21, Biochemistry for the reaction]

**(xv) Ans: (b) esters**

The reaction of carboxylic acid with alcohol produces an ester. This reaction is called esterification reaction.

**Q2: Write short answers**

**(I) What are aliphatic and aromatic carboxylic acids?**

Carboxylic acids are generally of two types

Aliphatic carboxylic acids and aromatic carboxylic acids

The general formula of aliphatic carboxylic acid is,



where R = H or an alkyl group

The general formula of aromatic carboxylic acid is



where Ar = phenyl or aryl group

**(II) Give probable mechanism of alkaline hydrolysis of an ester.**

**Step 1:**

The hydroxide nucleophile attacks at the electrophilic C of the ester  $\text{C}=\text{O}$ , breaking the  $\pi$  bond and creating the tetrahedral intermediate.

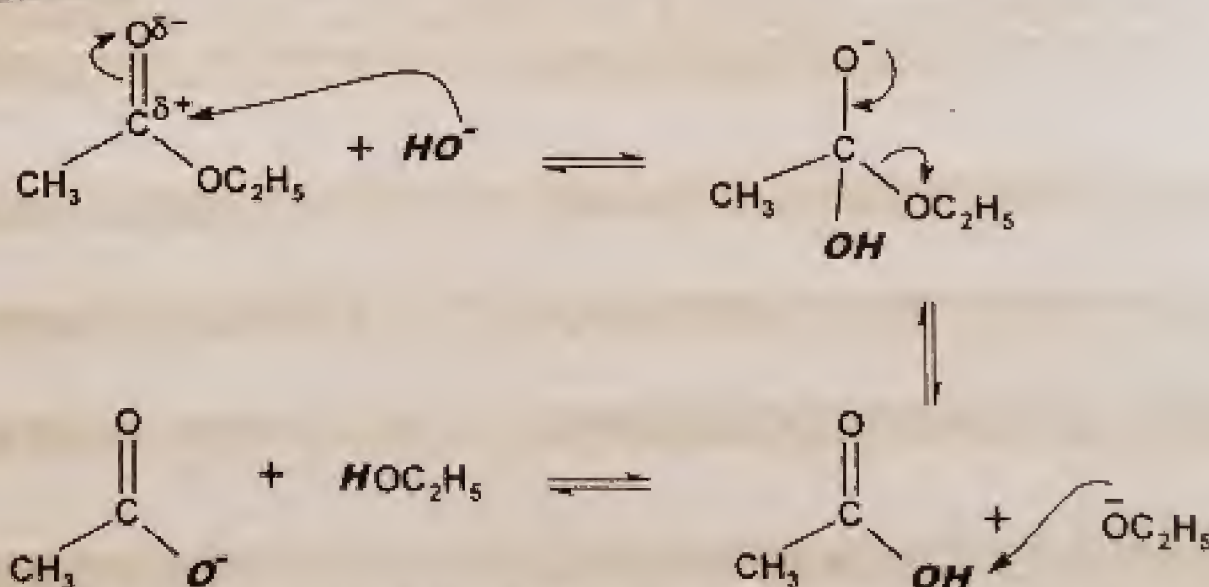
**Step 2:**

The intermediate collapses, reforming the  $\text{C}=\text{O}$

results in the loss of the leaving group the alkoxide,  $\text{RO}^-$ , leading to the carboxylic acid.

**Step 3:**

An acid / base reaction. A very rapid equilibrium where the alkoxide,  $\text{RO}^-$  functions as a base deprotonating the carboxylic



acid,  $\text{RCO}_2\text{H}$ , (an acidic work up would allow the carboxylic acid to be obtained from the reaction).



A carboxylic acid does not form phenyl hydrazone when treated with phenyl hydrazine. Explain

Hydrazine contains basic  $\text{NH}_2$  groups. This group accepts proton from carboxylic acid with the help of lone pair of electron on nitrogen atom. Since, lone pair has been used up. Moreover, the carbonyl group of carboxylic acids is less electrophilic. So hydrazine cannot attack as nucleophile on carboxylic acid. Thus, hydrazone is not formed.

Give the mechanism for the acid catalyzed hydrolysis of a nitrile?

Page 370

Why acetic acid is often called Glacial acetic acid?

Pure acetic acid freezes to an ice like solid at  $4^\circ\text{C}$ . Therefore it is called glacial acetic acid.

What is use of esters?

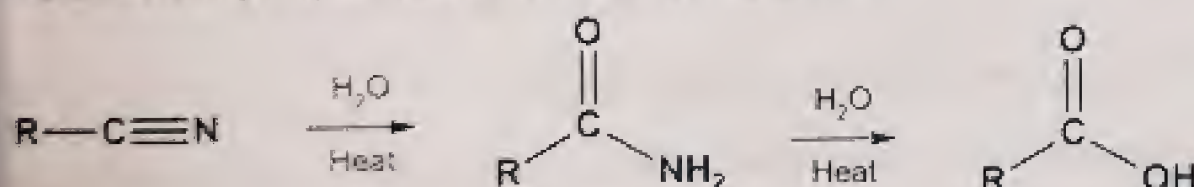
Esters have fruity smell. Thus they are used as artificial flavours.

Flavours of some esters are given below.

Ester	Flavour	Ester	Flavour
Amyl acetate	Banana	Isobutyl formate	Raspberry
Benzyl acetate	Jasmine	Ethyl butyrate	Pineapple
Amyl butyrate	Apricot	Octal acetate	Orange

How may nitriles be converted into carboxylic acid?

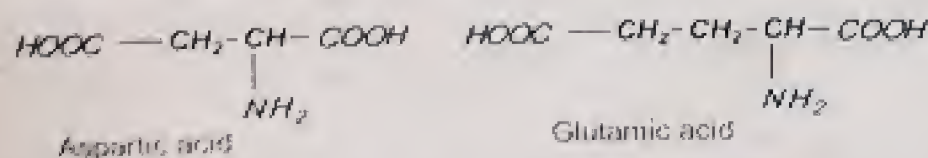
The nitriles on hydrolysis yield carboxylic acids via amides.



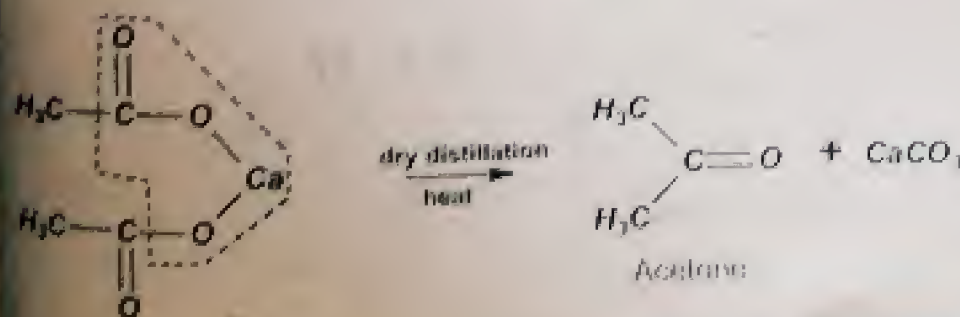
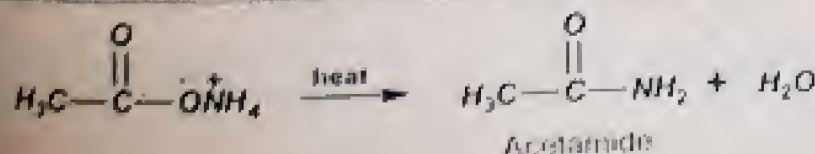
What are acidic amino acids give example?

Amino acids containing more carboxyl groups than amino group are called acidic amino acids.

Examples



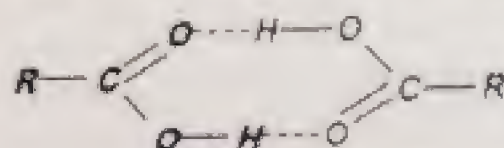
What happened when ammonium acetate and calcium acetate is heated.





(x) **How does carboxylic acids exist in nonpolar solvent**

The carboxylic acids exist as dimers in non-polar solvent like benzene. Thus, their Molecular mass appears to be twice of their actual mass.

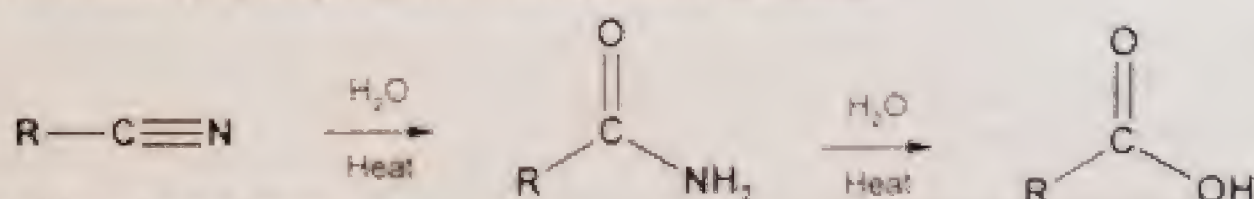


**Q3: Give detailed answers for the following questions.**

(i) **How will you prepare carboxylic acids from?**

(a) **alkyl nitrile**

The nitriles on hydrolysis yield carboxylic acids via amides.



(b) **Hydrolysis of esters**

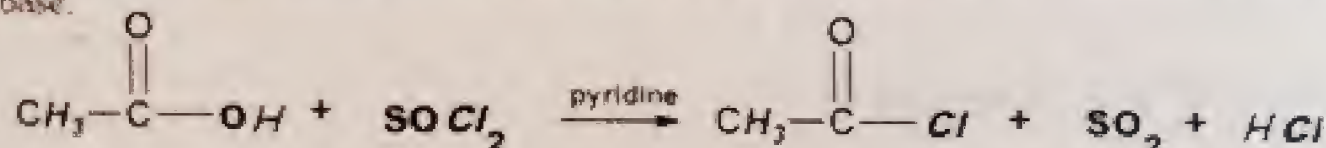
The ester on boiling with conc. sodium hydroxide gives sodium salt of the acid, which on treatment with dilute HCl gives free carboxylic acid.



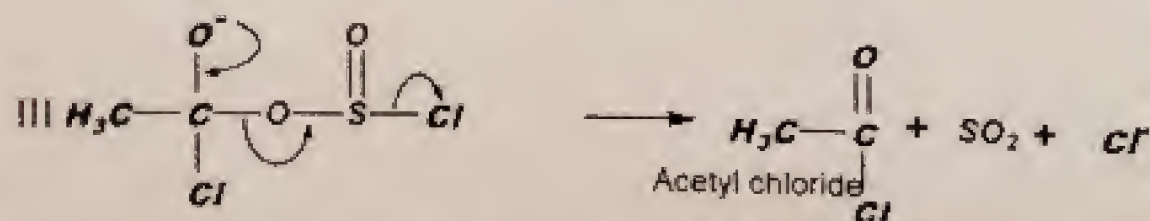
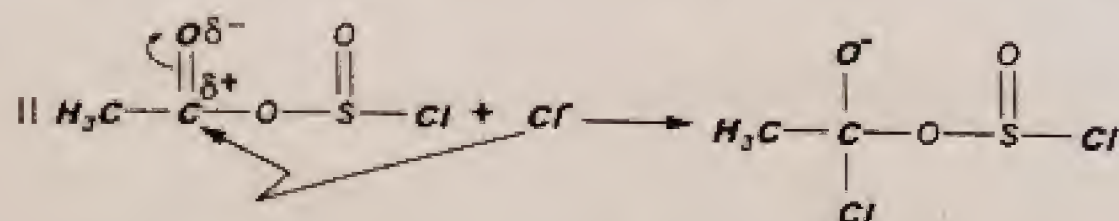
(ii) **Give the reaction of acetic acid with the following along mechanism:**

(a) **SOCl<sub>2</sub>**

Acyl chlorides are prepared by treating the carboxylic acid with thionyl chloride, SOCl<sub>2</sub>, in the presence of a base.

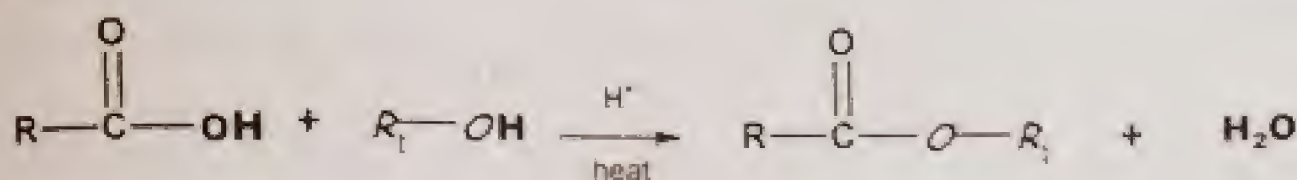


**Mechanism**





(b) Ethanol



Step 1:

An acid/base reaction. Protonation of the carbonyl makes it more electrophilic.

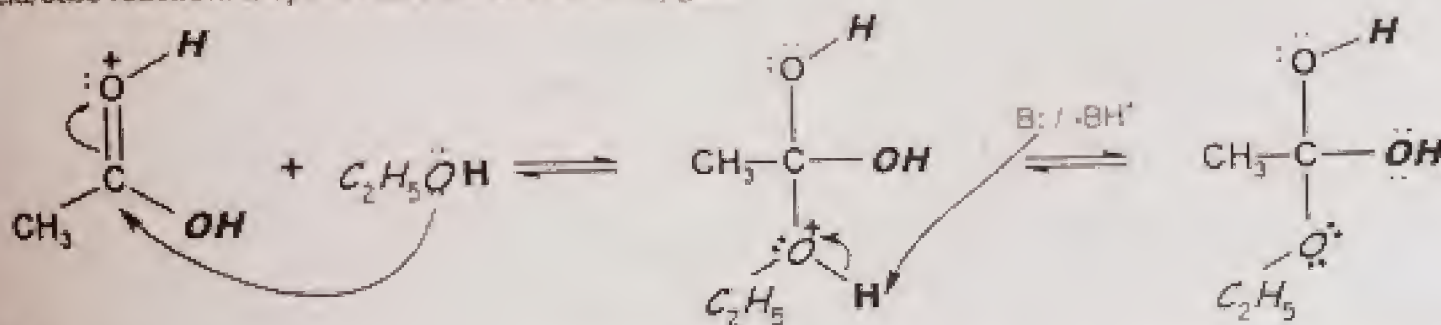


Step 2:

The alcohol O functions as the nucleophile attacking the electrophilic C in the C=O, with the electrons moving towards the oxonium ion, creating the tetrahedral intermediate.

Step 3:

An acid/base reaction. Deprotonate the alcoholic oxygen.



Step 4:

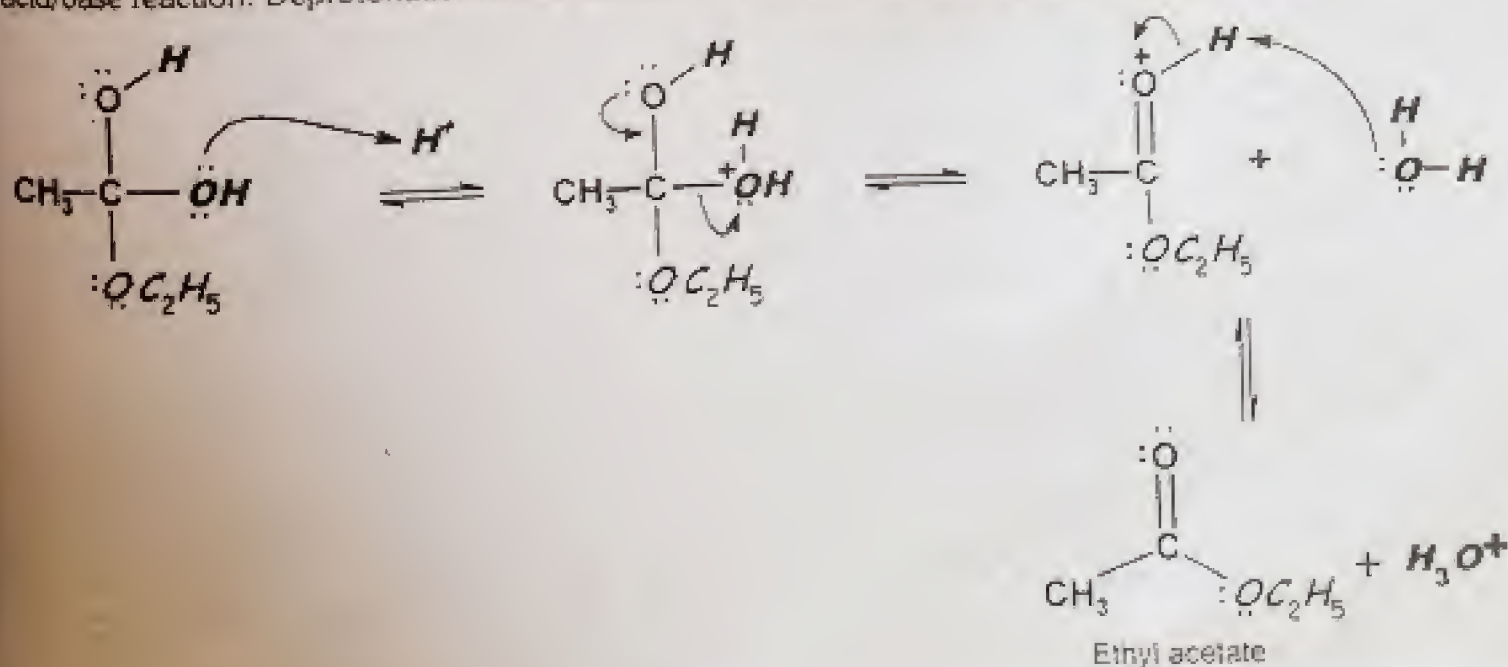
An acid/base reaction. Need to make an -OH leave, it doesn't matter which one, so convert it into a good leaving group by protonation.

Step 5:

Use the electrons of an adjacent oxygen to help "push out" the leaving group, a neutral water molecule.

Step 6:

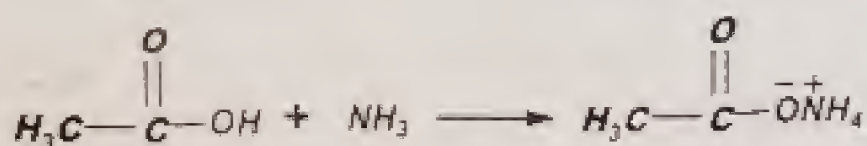
An acid/base reaction. Deprotonation of the oxonium ion reveals the carbonyl in the ester product.



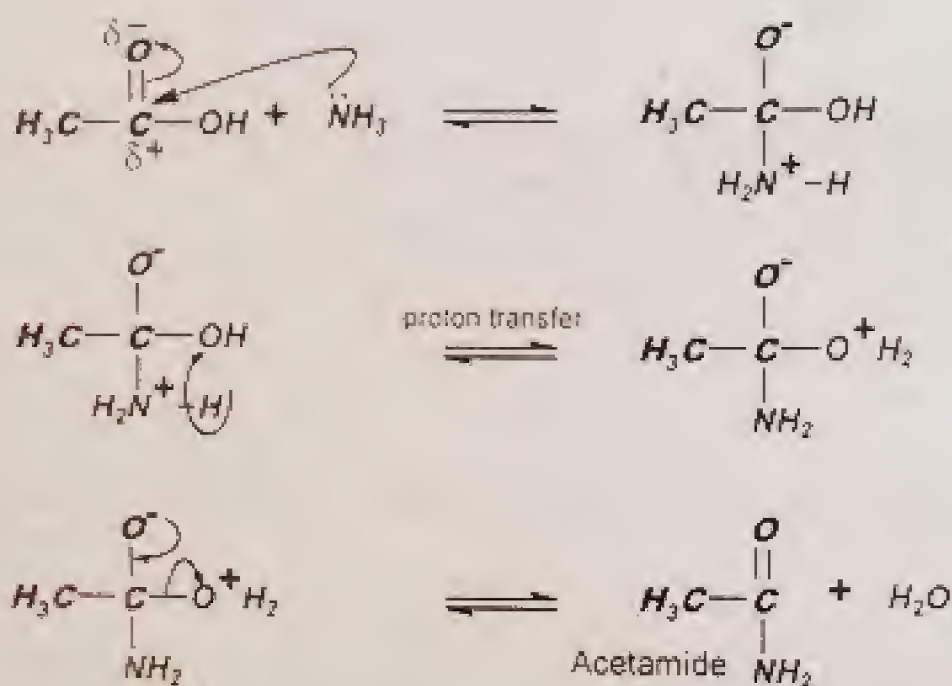


(c)  $\text{NH}_3$

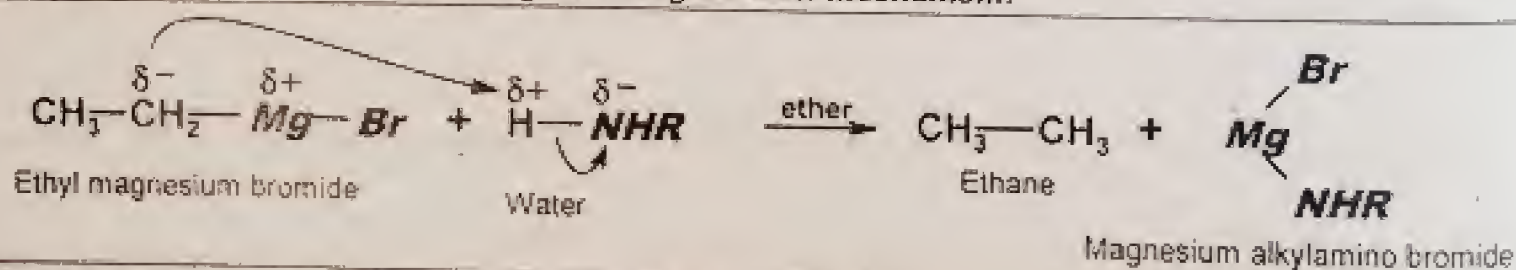
Carboxylic acids react with ammonia to form ammonium salts which on heating produce acid amides.



Mechanism

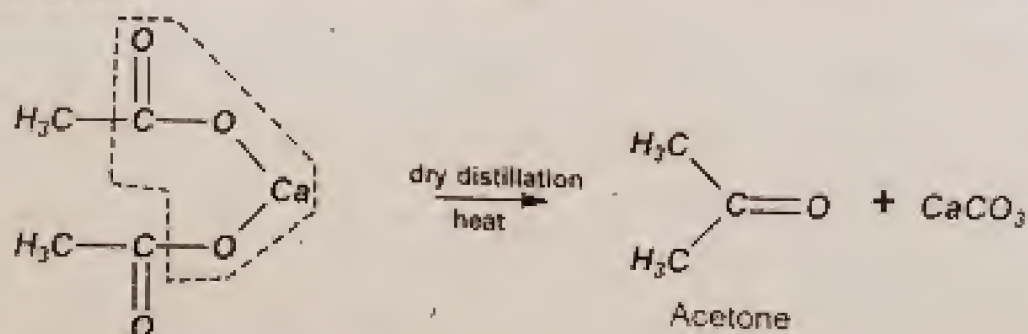


(iii) Give the reaction of amine with Grignard reagent with mechanism.

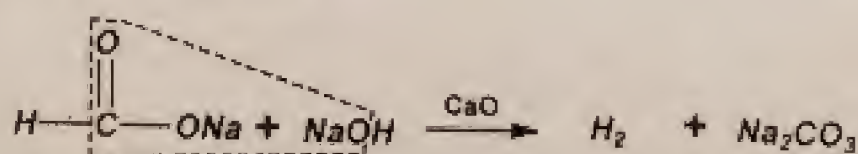


(iv) What happens when following compounds are heated;

(i) Calcium acetate



(ii) Sodium formate and soda lime









**TEST YOUR SKILLS**

Marks: 85

Time: 20 Minutes

**OBJECTIVE**

Marks: 17

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Q1. Circle the correct option i.e. A/B/C/D. Each part carries one mark.

- (i) Vinegar is  
A. 4-5 % acetic acid B. Glacial acetic acid C. Pure acetic acid D. Any one of these
- (ii) Which of the following is not a fatty acid?  
A. Phthalic acid B. Benzoic acid C. Phenyl acetic acid D. All of above
- (iii) In Fischer esterification, the reactivity order of alcohols is  
A.  $\text{CH}_3\text{OH} > 1^\circ > 2^\circ > 3^\circ$  B.  $1^\circ > 2^\circ > 3^\circ > \text{CH}_3\text{OH}$  C.  $3^\circ > 2^\circ > 1^\circ > \text{CH}_3\text{OH}$  D.  $\text{CH}_3\text{OH} > 3^\circ > 2^\circ > 1^\circ$
- (iv) Acetic acid at low temperature freezes and called  
A. 90% acetic acid B. Glacial acetic acid C. Semi solid acetic acid D. None of above
- (v) Which one of the following acid is used for the preparation of synthetic rubber  
A. Carbonic acid B. Formic acid C. Acetic acid D. Butyric acid
- (vi) 2-Hydroxy propanoic acid is called  
A. Oxalic acid B. Lactic acid C. Citric acid D. Aspartic acid
- (vii) Carboxylic acid on reduction with HI and red phosphorous gives  
A. Alkanes B. Alkenes C. Alkynes D. Alcohols
- (viii) The carbonation of Grignard's reagent is used to prepare  
A. acid halides B. amides C. carboxylic acids D. esters
- (ix) Which of the following do not contain  $-\text{COOH}$  group  
A. Picric acid B. P-toluene sulphonic acid C. Both D. None
- (x) An acid chloride compared with its acid boils at  
A. Low temperature B. Higher temperature C. Similar temperature D. An indefinite temperature
- (xi) Reaction between caustic soda and a fat is called  
(a) esterification (b) hydrogenation (c) neutralization (d) saponification  
A. Acidic amino acid B. Basic amino acid C. Neutral amino acid D. All of above
- (xii) The reduction of nitriles gives  
A. alcohols B. amines C. ester D. None
- (xiii) Which is the strongest acid?  
A.  $\text{Cl}_3\text{CCOOH}$  B.  $\text{HCOOH}$  C.  $\text{ClCH}_2\text{COOH}$  D.  $\text{CH}_3\text{COOH}$
- (xiv) The reduction of esters with  $\text{LiAlH}_4$  gives  
A. Amino acids B. amide C. alcohol D. alkane
- (xv) Which of the following derivative of carboxylic acids is the most reactive?  
A. acid halides B. amides C. anhydrides D. esters
- (xvi) Catalyst used for preparation of anhydride is  
A.  $\text{K}_2\text{Cr}_2\text{O}_7$  B.  $\text{H}_2\text{SO}_4$  C.  $\text{P}_2\text{O}_5$  D.  $\text{V}_2\text{O}_5$
- (xvii) The odour of esters is  
A. Pungent B. Suffocating C. Pleasant D. Fruity

**SUBJECTIVE**

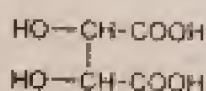
Time: 2:35 Hours

Total Marks Section B and C: 68

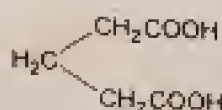
Section - B (Marks 42) ( $14 \times 3 = 42$ )

Q2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines.

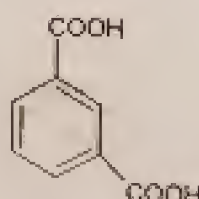
- (i) Name the following compounds according to IUPAC system



a.



b.



c.

03

- (ii) Acetic acid is a component of vinegar.

- a. How is Acetic acid manufactured from Acetylene?
- b. What is glacial acetic acid?

02  
01

- (iii) Esters formed carboxylic acids give different flavours. What type of flavours is given by Amylacetate, Isobutyl formate and Benzylacetate

03

- (iv) a. How is acetic acid prepared from alkyl nitriles?
- b. Give the mechanism for the reaction of acetic acid with  $\text{SOCl}_2$

01  
02



- (vi) Write the structural formula of the following. 03  
 a. Acrylonitrile      b. Acetophenone      c. Adipic acid
- (vii) What is Fisher esterification? Give mechanism. 03
- (viii) Predict the product of the following reactions:  
 a.  $\text{CH}_3\text{COOH} + \text{HI} \xrightarrow{\text{P}}$   
 b.  $\text{R}-\underset{\text{NH}_2}{\text{CH}}-\text{COOH} \xrightarrow[\text{HCl}]{\text{NaNO}_2}$   
 c.  $\text{CH}_3\text{COOH} + \text{NaHCO}_3 \longrightarrow$
- (ix) a. What are lactones? 01  
 b. Why methanoic acid is usually called formic acid? 01  
 c. Why low molecular mass carboxylic acids are water soluble, while high mol. mass are insoluble? 01
- (x) a. Write the reactivity order of functional derivatives of carboxylic acids. 1.5  
 b. What are acid anhydrides, how they are formed? 1.5
- (xi) a. Describe the acidity of carboxylic acids? 03
- (xii) a. How may amides be prepared? 01  
 b. Describe the mechanism of decarboxylation of dicarboxylic acids. 02
- (xiii) a. How ethanol is converted into acetic acid? 01  
 b. What is nucleophilic acyl substitution? Give example 02
- (xiv) a. What are dicarboxylic acids? 1.5  
 b. Describe the structure of a  $\text{COOH}$  group? 1.5
- (xv) a. How the acid by product such as  $\text{HCl}$  is removed from the solution? 1.5  
 b. Why acetic acid is often called glacial acetic acid? 1.5
- (xvi) a. Molecular mass of carboxylic acid appears double in a non-polar solvent. Why? 02  
 b. What happens when acid anhydrides are treated with alcohol 01
- (xvii) a. How  $\alpha$ -amino acids can be converted into  $\alpha$ -hydroxyl acids? 01  
 b. Write two chemical reactions in which carboxyl group of carboxylic acid is involved? 02
- (xviii) a. How would you convert acetic acid into Acetamide? 01  
 b. What happened when calcium acetate is heated? 01  
 c. How may nitriles be converted into carboxylic acid? 01
- (xix) How does acetic acid reacts with the following? 03  
 a. Methanol      b.  $\text{PCl}_5$       c.  $\text{LiAlH}_4$
- (xx) What happens when 01  
 a. Sodium metal is dropped in acetic acid 01  
 b. Sodium formate is heated at high temperature in presence of soda lime 01  
 c. What is oxonium ion?

### Section - C

**Note:** Attempt any TWO questions. All questions carry equal marks. (2 × 13 = 26)

- Q. 3. a. How will you prepare carboxylic acids from?  
 (i) Alkyl nitriles      (ii) Hydrolysis of esters

02



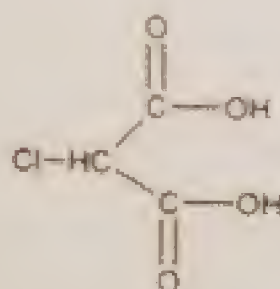
**CH # 20: Carboxylic acids and Functional Derivatives**

**386**

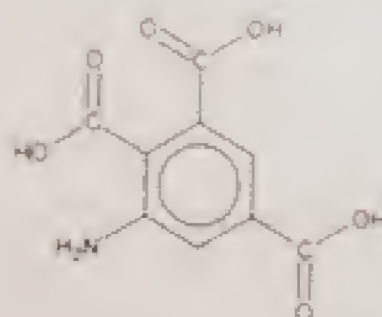
College Chemistry: Federal Board

- b. Give the reaction of acetic acid with the following along with mechanism  
(i)  $\text{SOCl}_2$  (ii) Ethanol (iii)  $\text{NH}_3$  06
- c. What type of laboratory methods and large scale methods are used for the preparation of acetic acid? 03
- d. How nitriles are prepared? 02
- Q. 4.** a. How would you convert Acetic acid into the following compounds? 04  
(i) Methane (ii) Ethanol (iii) Ethane (iv) Acetic anhydride
- b. Discuss structure and acidity of carboxylic acids 04
- c. Write formula and name of four functional derivatives of carboxylic acids? 04
- Q. 5.** a. Write the mechanism of reaction of a Grignard's reagent with a nitrile 04
- b. Give the IUPAC names of the following compounds 05

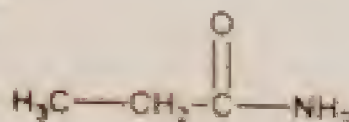
(i)



(ii)



(iii)



(iv) Adipic acid

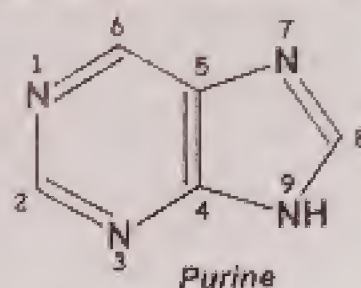
(v) Valeric acid

- c. How many acid halides be converted into different functional derivatives of carboxylic acids. 04



## CHAPTER # 21

# BIOCHEMISTRY



### INTRODUCTION TO BIOCHEMISTRY

Biochemistry is the branch of science concerned with studying the various molecules that occur in living cells and organisms, with their chemical reactions.

- Biochemistry is a hybrid science.
- Biology is the science of living organisms and chemistry is the science of atoms and molecules, so biochemistry is the science of the atoms and molecules in living organisms.
- Biochemistry is concerned with the complete spectrum of all forms of life. It covers from relatively simple viruses and bacteria to complex human beings.
- It attempts to describe the structures, mechanisms and chemical processes shared by all organisms on molecular level.
- Living organisms should be able to transform matter and energy into different forms, show response to changes in their environment and show growth and reproduction.

### MACROMOLECULES

Molecules containing large number of atoms and high molecular mass are called macromolecules.

- All living organisms undergo changes due to large organic compounds called macromolecules.
- Four main types of macromolecules control all activities. They are carbohydrates, proteins, lipids and nucleic acids.

### CARBOHYDRATES

#### Old Definition

Carbohydrates are called carbohydrates because they contain carbon, oxygen and hydrogen and these are generally in proportion to form water with the general formula  $C_n(H_2O)_n$ .

#### Modern Definition:

Carbohydrates are polyhydroxy compounds of aldehydes or ketones.

#### Remember!

- All the organic compounds containing hydrogen and oxygen in the proportion of 2:1 are not carbohydrates.

e.g.

- |                   |                                |
|-------------------|--------------------------------|
| (i) Formaldehyde  | $HCHO = C(H_2O)$               |
| (ii) Acetic acid  | $CH_3COOH = C_2(H_2O)_2$       |
| (iii) Lactic acid | $CH_3CH(OH)COOH = C_3(H_2O)_3$ |

On the other hand, Rhamnose ( $C_6H_{12}O_5$ ) does not have the ratio of hydrogen to oxygen as in  $HO$ , but it is a carbohydrate.

#### Importance of Carbohydrates

- Carbohydrates or saccharides are the most abundant of the four types of macromolecules.
- These are sugars or starches.
- They have several roles in living organisms, including energy transportation as well as being structural components of plants and arthropods.
- Carbohydrate derivatives are actively involved in fertilization, immune systems, development of disease, blood clotting and growth.



- Most organic matter on earth is made up of carbohydrates because they are involved in so many aspects including:
  - ✓ Energy stores, fuels, and metabolic intermediaries.
  - ✓ Ribose and deoxyribose sugars are part of the structural framework of RNA and DNA.
  - ✓ The cell walls of bacteria are mainly made up of polysaccharides (types of carbohydrate).
  - ✓ Cellulose (a type of carbohydrate) makes up most of plant cell walls.
  - ✓ Carbohydrates are linked to many proteins and lipids (fats), where they are vitally involved in interactions.

## CLASSIFICATION OF CARBOHYDRATES

**Exercise Q3 (I):** Describe different classes of Carbohydrates.

Carbohydrates are classified into three types.

### MONOSACCHARIDES

**Definition:** The carbohydrates which do not hydrolyze to simpler units are called monosaccharides. This is the smallest possible sugar unit.

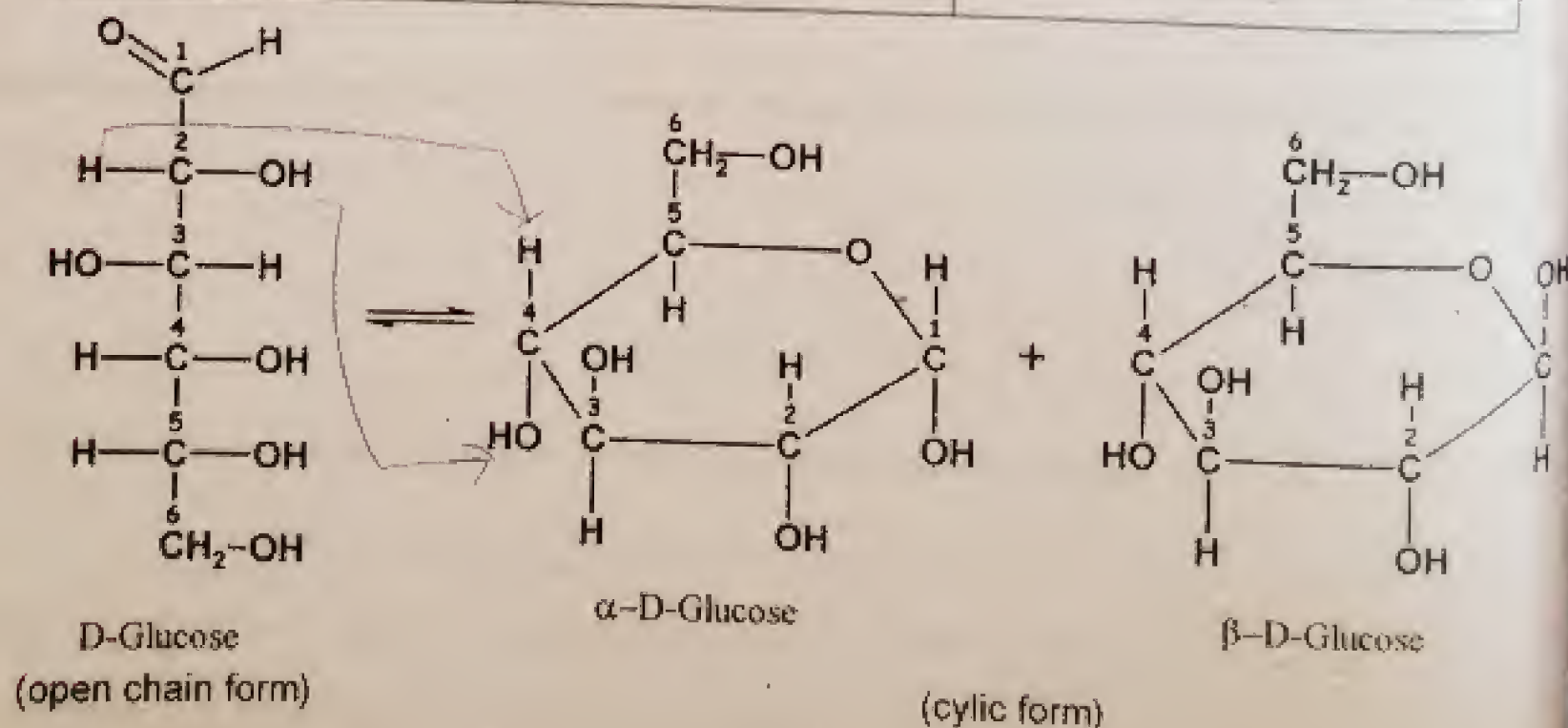
- The term blood sugar refers to glucose in the blood.
- Glucose is a major source of energy for a cell.
- Glucose is naturally in honey and corns.
- In human nutrition, galactose can be found most readily in milk and dairy products.
- Fructose is found mostly in vegetables and fruits (grapes).
- When monosaccharides join together in linked groups, they are called polysaccharides.

**Examples:** glucose, galactose or fructose.

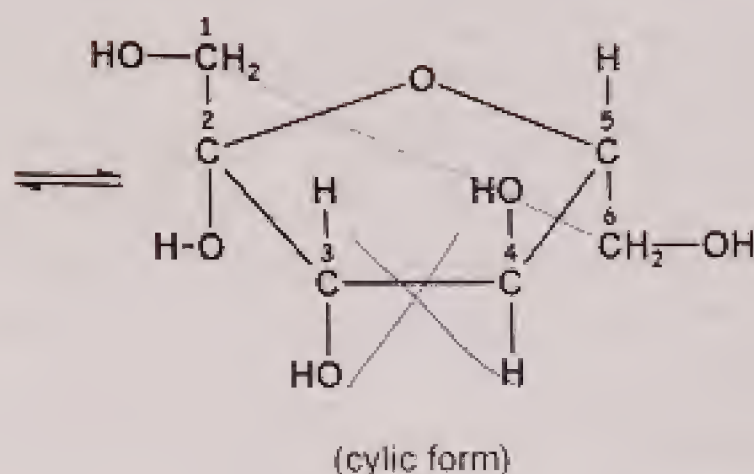
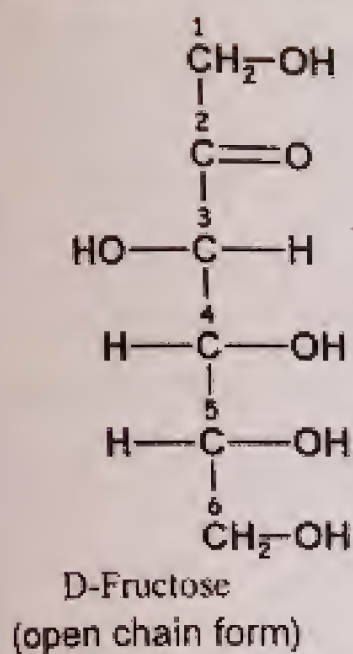
### CLASSIFICATION OF MONOSACCHARIDES

- Monosaccharides can be further classified by the number of carbons present.
- Among these hexoses (6-carbons) are most common.

Six = Hexose	Number of Carbons Five = Pentose	Three = Triose
Glucose	Ribose	Glyceraldehyde
Galactose		
Fructose		







## DISACCHARIDES

**Definition:** Carbohydrate producing two monosaccharide units on hydrolysis are called disaccharides.

- In these two monosaccharide molecules are bonded together to form disaccharides.
- Disaccharides are polysaccharides. The term "poly" specifies any number higher than one, while "di" specifies exactly two.

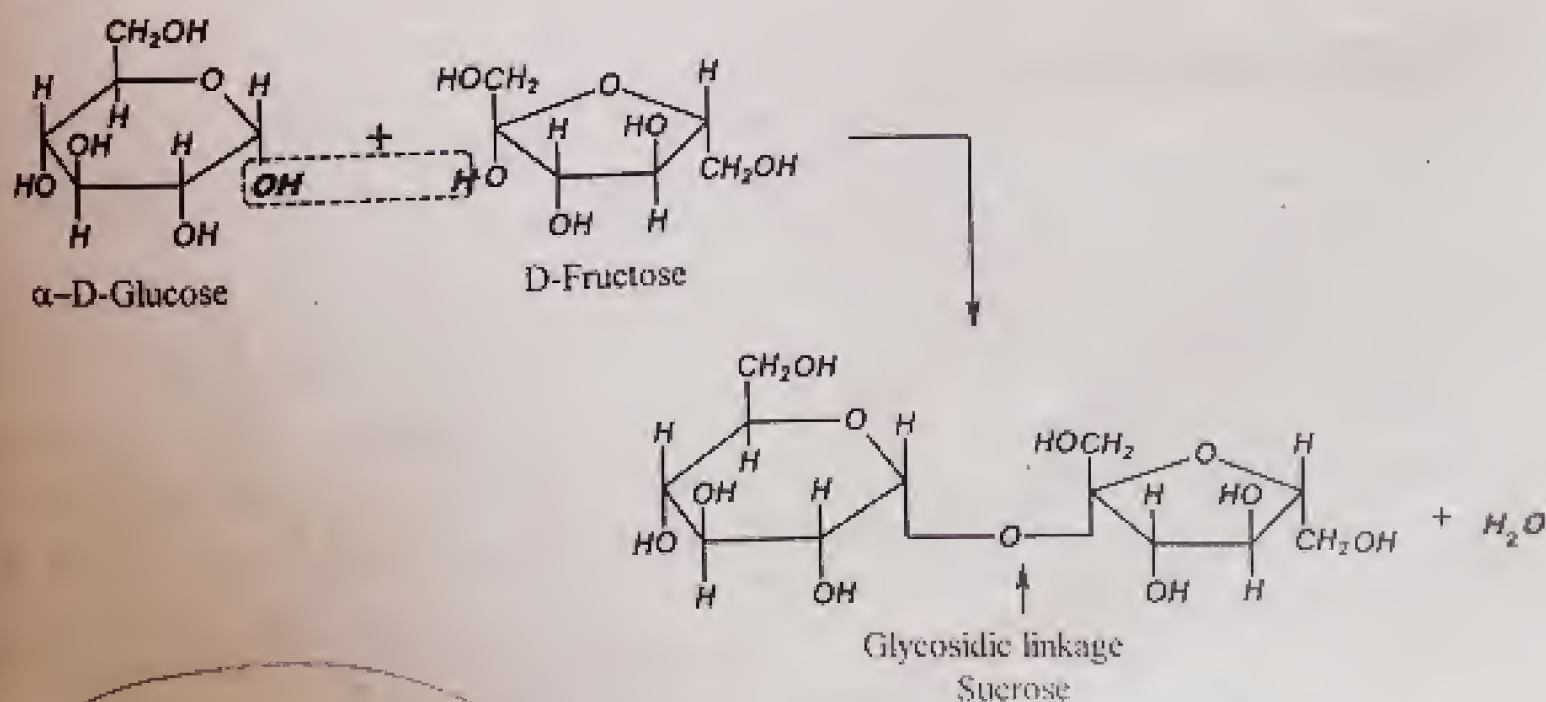
**Examples:** lactose, maltose, and sucrose.

**Occurrence:**

- Lactose is formed in the milk
- Sucrose occurs in sugarcane, sugar beet, mango, pineapple, almond and apricot.

**How the monosaccharides combine with each other:**

The OH group of one monosaccharide molecule acts as alcohol. It forms a glycosidic linkage with the hemiacetal group of second monosaccharide molecule. In this way, glucoside is produced which is called disaccharide. Thus, disaccharides are the acetals formed from two monosaccharides by the elimination of one molecule of  $\text{H}_2\text{O}$  molecule as shown below.



If one glucose molecule is bonded with a galactose molecule, lactose is formed, which is commonly found in milk.



## POLYSACCHARIDES

**Definition:** The carbohydrates producing large number of mono-saccharides on hydrolysis are called polysaccharides.

- It is a chain of two or more monosaccharides. The chain may be branched (molecule is like a tree with branches and twigs) or unbranched (molecule is a straight line with no twigs).
- Polysaccharide molecule chains may be made up of hundreds or thousands of monosaccharides.
- Polysaccharides are polymers. A simple compound is a monomer, while a complex compound is a polymer which is made of two or more monomers.

**Examples:** Starch, cellulose etc

A brief summary is presented below;

Monosaccharides	Carbohydrates Disaccharides	Polysaccharides
Glucose	Sucrose	Starch
Galactose	Maltose	Glycogen
Fructose	Lactose	Cellulose
Ribose		
Glyceraldehyde		

### Interesting Information

A new system for classifying carbohydrates is the glycemic index. The glycemic index ranks foods on how they affect blood sugar level by measuring how much the blood sugar increases after one eats.

## FUNCTIONS OF CARBOHYDRATES

The main functions of carbohydrates are given below:

- They are source of energy. Thus, they spare protein so that protein can concentrate on building, repairing, and maintaining body tissues instead of being used up as an energy source.
- For proper fat metabolism, carbohydrates must be present. If there are not enough carbohydrates, then large amounts of fat are used for energy. The body is not able to handle this large amount so quickly, so it accumulates ketone bodies, which make the body acidic. This causes a condition called ketosis.
- Carbohydrate is necessary for the regulation of nerve tissue. These are the only source of energy for the brain.
- Certain types of carbohydrates support the growth of healthy bacteria in the intestines for digestion.
- Some carbohydrates are high in fibre. These help prevent constipation. These also lower the risk for certain diseases such as cancer, heart disease and diabetes.
- Polysaccharides act as food stores in plants in the form of starch, or in humans and other animals in the form of glycogen.
- Polysaccharides also have structural roles in the plant cell wall in the form of cellulose or pectin, and the tough outer skeleton of insects in the form of chitin.



**THREE MAJOR FUNCTIONS OF CARBOHYDRATES**

Three major functions of polysaccharides are discussed below.

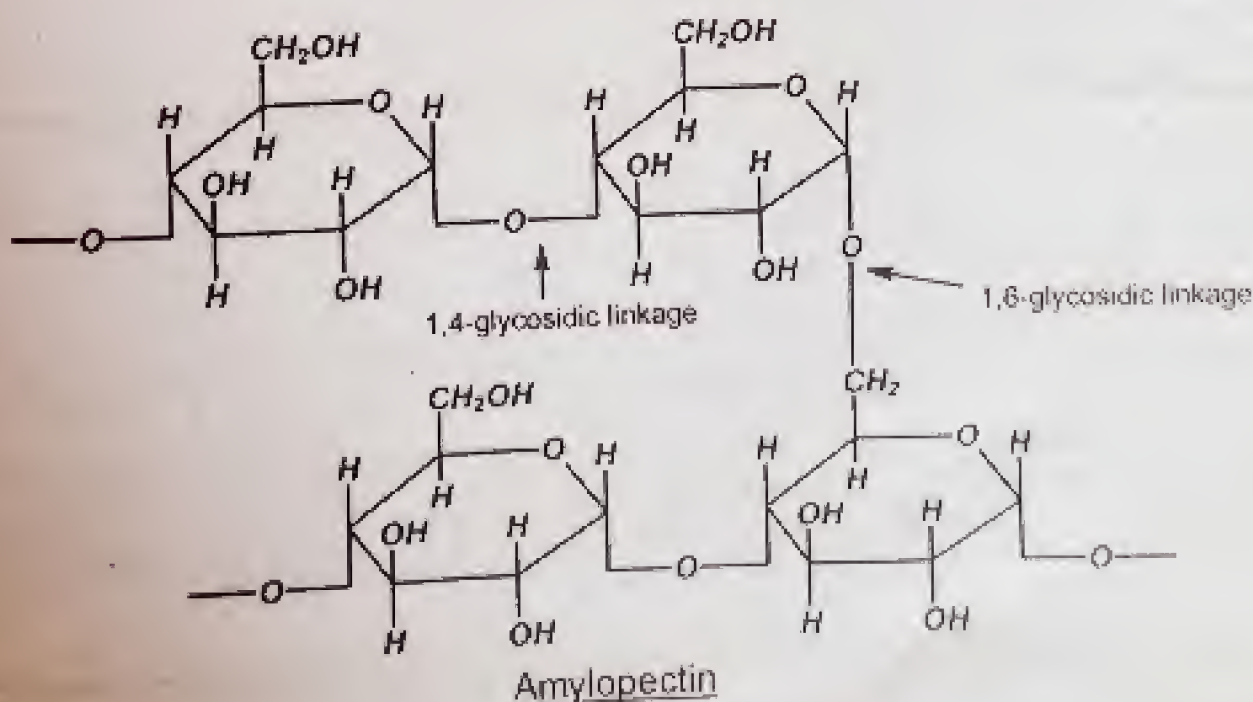
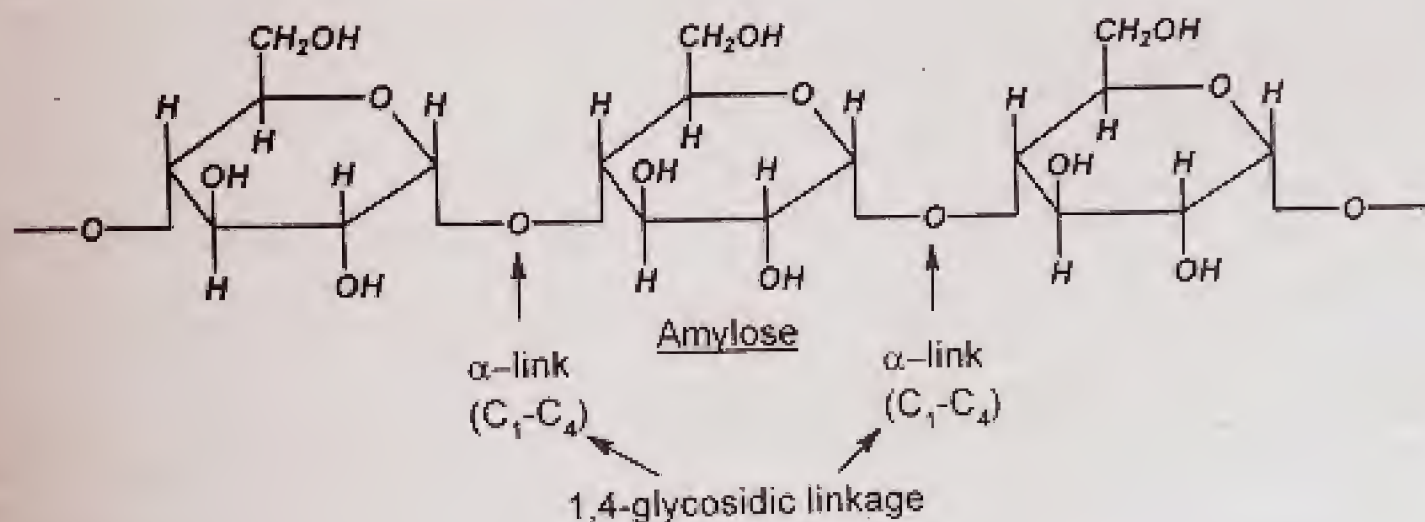
**(I) STORAGE POLYSACCHARIDES****Glycogen:**

- The carbohydrates are stored as glycogen in humans and animals.
- It is a polysaccharide that is stored in the liver and muscles.

**Starch:**

- These are glucose polymers made up of Amylose (10-20%) and Amylopectin (80-90%).
- Starches are water insoluble.
- Humans and animals digest them by hydrolysis. Our bodies have amylases which break them down.
- Rich sources of starches for humans are potatoes, rice and wheat.

Structures of Amylose and Amylopectin are given below

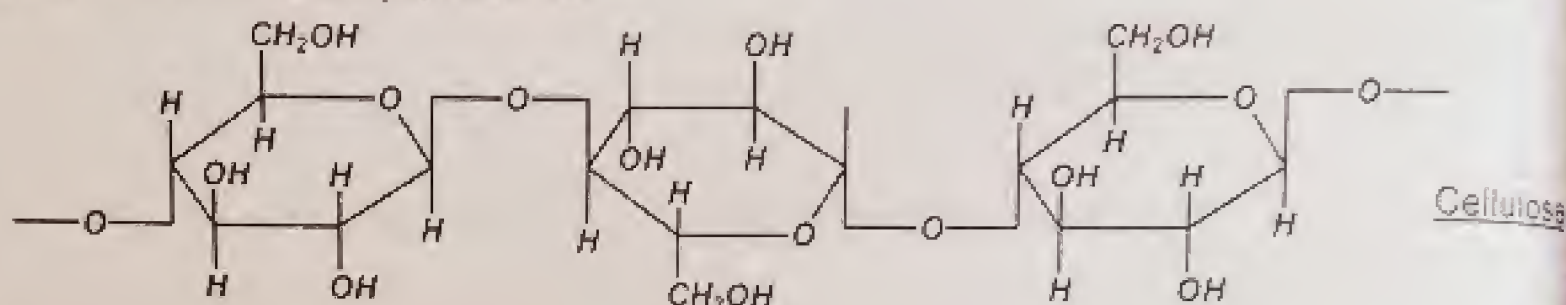




## (2) STRUCTURAL POLYSACCHARIDES

### Cellulose:

- The structural constituents of plants are made mainly from cellulose. It is a type of polysaccharide.
- Wood is mostly made of cellulose,
- Paper and cotton are almost pure cellulose.



### Chitin:

- It is one of the most abundant natural materials in the world.
- Microorganisms, such as bacteria and fungi secrete chitinases, which over time can break down chitin.
- Chitin is the main component of fungi cell walls, the exoskeletons (hard outer shell/skin) of arthropods, such as crabs, lobsters, ants, beetles, and butterflies.

## (3) BACTERIAL POLYSACCHARIDES

- They are found in bacteria, especially in bacterial capsules.
- Pathogenic bacteria often produce a thick layer of mucous-like polysaccharide. This layer protects the bacteria from the host's immune system.
- Thus, if the bacteria are in a human, then human's immune system would less likely attack the bacteria because the polysaccharide layer covers its pathogenic properties.

## NUTRITIONAL IMPORTANCE OF CARBOHYDRATES

- Scientific research has shown the diverse functions of carbohydrates in the body and their importance for good health.
- Bread, pasta, beans, potatoes, bran, rice and cereals are carbohydrate-rich foods.

### Remember!

- 1 gram of carbohydrate contains approximately 4 kilocalories (kcal)
- 1 gram of protein contains approximately 4 kcal
- 1 gram of fat contains approximately 9 kcal

## (A) BODY WEIGHT REGULATION

People eating a diet high in carbohydrates are less likely to accumulate body fat compared with those who follow a low carbohydrate/high-fat diet.

It is due to three reasons

- It could be due to the lower energy density of high carbohydrate diets, as carbohydrates have fewer calories than fats. Fiber-rich foods also tend to be bulky and physically filling, so fewer calories may be consumed.
- Studies show that carbohydrates, both in the form of starch and sugars, work quickly to aid satiety and that those consuming high carbohydrate diets are therefore less likely to overeat.
- It is evident that diets high in carbohydrate, as compared with those high in fat, reduce the likelihood of developing obesity.

### Interesting Information

- In several studies, high sugar consumers have been found to be slimmer than low sugar consumers.
- **Obesity** means having too much body fat.



**(B) DIABETES**

- There is no evidence that sugar consumption is linked to the development of any type of diabetes.
- There is now a good evidence that obesity and physical inactivity increase the likelihood of developing non-insulin dependent diabetes, which usually occurs in middle age.
- Weight reduction is usually necessary and is the primary dietary aim for people with non-insulin dependent (Type II) diabetes.
- Consuming a wide range of carbohydrate foods is an acceptable part of the diet of all diabetics, and the inclusion of low glycaemic index foods is beneficial as they help to regulate blood glucose control.
- Most recommendations for the dietary management of diabetes allow a modest amount of ordinary sugar as the inclusion of sugar with a meal has little impact on either blood glucose or insulin concentrations in people with diabetes.

**(C) DENTAL HEALTH****Factors Affecting Tooth Decay**

The incidence of tooth decay is influenced by a number of factors. These include:

- degree of oral hygiene and plaque removal carried out,
- availability of fluoride,
- type of food eaten,
- frequency of consumption of any fermentable carbohydrate
- genetic factors

**Role of Carbohydrates in Tooth Decay**

- Foods containing sugars or starch can be broken down by the enzymes and bacteria in the mouth. This produces acid which attacks the enamel of the teeth.
- The important thing is the often use of carbohydrate not the amount of sugar or other carbohydrate.
- After an acid challenge, saliva provides a natural repair process which rebuilds the enamel.
- When carbohydrate-containing foods are consumed too frequently, or chewed over time, this natural repair process is overcome by the tooth decay process. Thus, the risk of tooth decay is increased.

**(D) GETTING ACTIVE**

- There is now substantial evidence that carbohydrates can improve the performance of athletes.
- During high intensity exercise, carbohydrates are the main fuel for the muscles.
- By consuming high levels of carbohydrate before, during and after training or an event, glycogen stores are kept well stocked. These stocks help the athlete to perform for longer and help their bodies sustain the effort.
- The vital role of physical activity in maintaining health and fitness in the general population is now recognized. There is no doubt that many people would benefit from increasing their Activity level as it helps in the regulation of body weight. It also reduces the risk of developing diseases such as heart disease and diabetes. For those who want to keep fit and active, a well-balanced high-carbohydrate diet is recommended.

**QUICK QUIZ-1**

(1) What are carbohydrates? Give its general formula.

**Old Definition**

Carbohydrates are called carbohydrates because they contain carbon, oxygen and hydrogen and these are generally in proportion to form water with the general formula  $C_n(H_2O)_n$ .

**Modern Definition:**

Carbohydrates are polyhydroxy compounds of aldehydes or ketones. According to modern concept, they cannot be assigned some general formula.



(2) Quote one example of each type of carbohydrates.

Carbohydrates are classified into three types.

**Monosaccharides:** e.g. glucose, galactose, fructose.

**Disaccharides:** e.g. lactose, maltose, sucrose.

**Polysaccharides:** e.g. starch, cellulose.

(3) Write structural formulae of Glucose and Fructose.

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(4) What do you understand by glycemic index?

It is a new system for classifying carbohydrates is the glycemic index.

The glycemic index ranks foods on how they affect blood sugar level by measuring how much the blood sugar increases after one eats.

(5) How much calories do 1gm of carbohydrate have?

1 gram of carbohydrate contains approximately 4 kilocalories (kcal)

(6) On what factors tooth decay depend?

The incidence of tooth decay is influenced by a number of factors. These include:

- degree of oral hygiene and plaque removal carried out,
- availability of fluoride,
- type of food eaten,
- frequency of consumption of any fermentable carbohydrate
- genetic factors

## PROTEINS

**Definition:** The molecules which yield amino acids on complete hydrolysis are called Proteins.

- Proteins are probably the most important class of biochemical molecules, although of course lipids and carbohydrates are also essential for life.
- Proteins are the basis for the major structural components of animal and human tissue.
- Proteins are natural polymer molecules consisting of amino acid units. The number of amino acids in proteins may range from two to several thousand.
- These molecules contain nitrogen, carbon, hydrogen and oxygen.
- They act as biological catalysts (enzymes), form structural parts of organisms, participate in cell signal and recognition factors, and act as molecules of immunity. Proteins can also be a source of fuel.

## CLASSIFICATION OF PROTEINS

Three classes of proteins are usually defined.

### A. Simple Proteins:

**Definition:** Those which give one amino acid only, upon hydrolysis.

**Examples:**

- **Albumins:**
  - ✓ blood (serumalbumin); milk (lactalbumin); egg white (ovalbumin); lentils (legumelin); kidney bean (phaseolin); wheat (leucosin).
  - ✓ Globular protein is soluble in water and dilute salt solution.
  - ✓ It is precipitated by saturation with ammonium sulfate solution.
  - ✓ It is coagulated by heat.
  - ✓ It is usually found in plant and animal tissues.



• **Globulins:**

- ✓ blood (serum globulins); muscle (myosin); potato (tuberin); Brazil nuts (excelsin); hemp (edestin); lentils (legumin).
- ✓ Globular protein is sparingly soluble in water and soluble in neutral solutions.
- ✓ It is precipitated by dilute ammonium sulfate.
- ✓ It is coagulated by heat.
- ✓ It is distributed in both plant and animal tissues.

• **Glutelins:**

- ✓ Wheat (glutenin); rice (oryzenin).
- ✓ It is insoluble in water and dilute salt solutions.
- ✓ It is soluble in dilute acids.
- ✓ It is found in grains and cereals.

• **Histones:**

- ✓ thymus gland, pancreas and nucleoproteins (nucleohistone).
- ✓ It is soluble in water, salt solutions and dilute acids.
- ✓ It is insoluble in ammonium hydroxide.
- ✓ It yields large amounts of lysine and arginine.
- ✓ It is present combined with nucleic acids within cells.

• **Scleroproteins:**

- ✓ connective tissues and hard tissues.
- ✓ Fibrous protein is insoluble in all solvents.
- ✓ It is resistant to digestion.

**B. CONJUGATED PROTEINS:**

**Definition:** Those which give an amino acid and non-protein group upon hydrolysis

**Examples:**

• **Nucleoproteins:**

- ✓ cytoplasm of cells (ribonucleoprotein), nucleus of chromosomes (deoxyribonucleoprotein), viruses and bacteriophages.
- ✓ It contains nucleic acids, nitrogen and phosphorus.
- ✓ It is present in chromosomes and in all living forms as a combination of protein with either DNA or RNA.

• **Mucoprotein:**

- ✓ saliva (mucin) and egg white (ovomucoid).
- ✓ Proteins combined with amino sugars, sugar acids and sulfates.

• **Glycoprotein:**

- ✓ bone (osseomucoid), tendons (tendomucoid) and cartilage (chondromucoid).
- ✓ If it contains more than 4% then hexosamine, mucoproteins;
- ✓ If less than 4%, then glycoproteins.

• **Phosphoprotein:**

- ✓ milk (casein) and egg yolk (ovovitellin).
- ✓ Phosphoric acid joined in ester linkage to protein.



**C. DERIVED PROTEINS:**

**Definition:** Those which are derived from simple and conjugated proteins

**Examples:**

- **Proteans:**
  - ✓ edestan (from elastin) and myosin (myosin).
  - ✓ It results from short action of acids or enzymes.
  - ✓ It is insoluble in water.
- **Proteases:**
  - ✓ Intermediate products of protein digestion.
  - ✓ It is soluble in water.
  - ✓ It is not coagulated by heat.
  - ✓ It is precipitated by saturated ammonium sulfate.
  - ✓ It results from partial digestion of protein by pepsin or trypsin.
- **Peptones:**
  - ✓ intermediate products of protein digestion.
  - ✓ It has the same properties as proteases except that they can not be salted out.
  - ✓ It is of smaller molecular weight than proteases.
- **Peptides:**
  - ✓ intermediate products of protein digestion.
  - ✓ Two or more amino acids joined by a peptide linkage.
  - ✓ It is hydrolyzed to individual amino acids.

**STRUCTURE OF PROTEINS**

**Exercise Q3 (II): Explain the structure of Proteins.**

The structure of a protein depends upon the spatial arrangement of polypeptide chains present in proteins

Since three spatial arrangements are possible, proteins have the following structures.

- (A) Primary structure
- (B) Secondary structure
- (C) Tertiary structure
- (D) Quaternary structure

**Quick Quiz-2 (2): Differentiate primary, secondary and tertiary structure of Proteins.**

**(A) THE PRIMARY STRUCTURE OF PROTEINS**

- The sequence of amino acids in a peptide chain is called primary structure.
- Amino acids are linked with one another through peptide bond. The arrangement of these acids is called primary structure.

**(B) THE SECONDARY STRUCTURE OF PROTEINS**

- Peptide chains may acquire spiral shape or may be present in a zig-zag manner. This coiling or zig-zagging of polypeptide is called secondary structure of protein.
- It is due to the formation of H-Bonds.



**THE TERTIARY STRUCTURE OF PROTEINS**

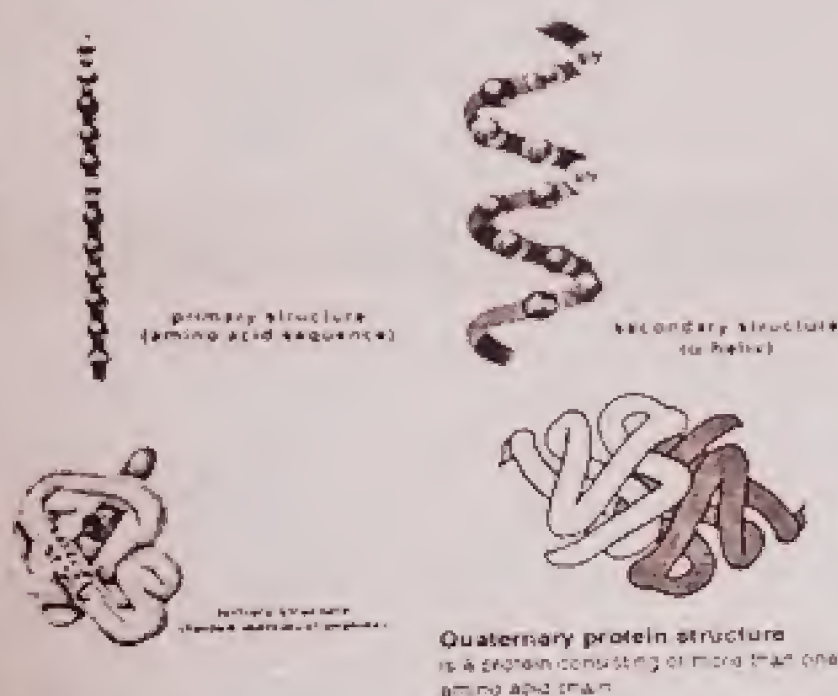
Twisting or folding of polypeptide chains represents tertiary structure of proteins

**QUATERNARY PROTEINS**

Quaternary means four. This is the fourth phase in the creation of a protein.

Quaternary protein is the arrangement of multiple folded protein or coiling protein molecules in a multi-subunit complex.

A variety of bonding interactions including hydrogen bonding, salt bridges, and disulfide bonds hold the various chains into a particular geometry.

**PROPERTIES OF PROTEINS**

- (1) Proteins are one of the four major groups of macromolecules that are found in all living organisms.
- (2) These giant molecules carry out many of the vital functions needed by cells.
- (3) Proteins are involved in such processes as food digestion, cell structure, catalysis, movement, energy manipulation and much more.
- (4) They are complex, huge associations of molecular subunits that appear impossibly difficult to understand.
- (5) Fortunately they are all built using the same construction principle.
- (6) As with all macromolecules, proteins are polymers, composed of smaller subunits - the amino acids - joined together in long chains.
- (7) There are about 20-22 common amino acids found in most proteins. All but one of these small molecules has the same common structure, but varies in the nature of one chemical group - termed the "R-group".
- (8) It is the varying structure and properties of these R-groups that make amino acids different from one another.
- (9) Amino acids are joined together in long chains called "polypeptides", a name which comes from the type of bond holding the chains of amino acids together. The group of atoms that hold the amino acids together is called a peptide bond. The order, or sequence of amino acids along a polypeptide chain establishes the first critical property of proteins, its primary structure.



## IMPORTANCE OF PROTEINS

Following are the features of the protein in they are thought to be very important:

- (1) Proteins play an important role in the formation of protoplasm. Protoplasm is the essence of all form of life.
- (2) Nucleoproteins are complex proteins and act as the carrier of heredity from one generation to the other.
- (3) Enzymes are the biological catalyst and they are also proteins. Without enzymes life is not possible.
- (4) Hemoglobin is a protein. It acts as carrier of oxygen.
- (5) Some of the proteins act as hormones. They carry out the regulatory function of the body.
- (6) Proteins have great importance in industry. The tanning of hides is an industrial process. This process is precipitation of protein by tannic acid.
- (7) Gelatin is obtained by heating bones, skins and tendons in water. It is used in bakery goods.
- (8) Casein is another protein used in the manufacture of buttons and buckles.
- (9) Proteins obtained from the soyabean are used for the manufacture of plastics.

## QUICK QUIZ-2

- (1) What are proteins? Give its simple classifications.

The molecules which yield amino acids on complete hydrolysis are called Proteins.

Proteins are classified into three types

**Simple Proteins:** e.g. Albumins; Globulins; Histones;

**Conjugated proteins:** e.g. Nucleoproteins; Glycoprotein;

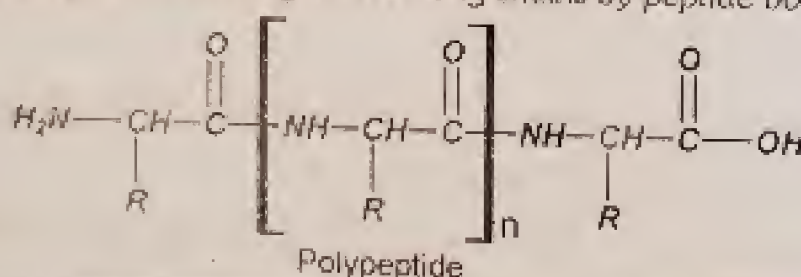
**Derived proteins:** e.g. Proteases; Peptones;

- (2) Differentiate primary, secondary and tertiary structure of Proteins.

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- (3) What are polypeptides?

When amino acids are joined together in long chains by peptide bond, then the compound is called polypeptide.



## ENZYMES (Greek word En means in and Zyme means yeast)

**Definition:** Enzymes are biocatalysts which alter the speed of metabolic activities in the living bodies.

Enzymes are complex protein molecules which are quite specific in action and sensitive to temperature and pH.

## ROLE OF ENZYMES AS A BIOCATALYST

The life of living organisms is a reflection of what is going on in their bodies.

- **Metabolism:** It is the set of biochemical reactions that occur in living organisms in order to maintain their environments. It is of two types.
  - ✓ **Anabolism:** It includes the biochemical reactions in which larger molecules are synthesized.
  - ✓ **Catabolism:** It includes the biochemical reactions in which larger molecules are broken down. Usually, energy is released in **catabolism** and it is utilized in anabolism. In this way biochemical reactions are actually energy transfers.
- During metabolism, chemicals are transformed from one form to the other by enzymes.



- Enzymes act as **biocatalysts** and speed up and regulate metabolic pathways.
- Enzymes are proteins that catalyze (i.e. speed up) biochemical reactions. These are not changed during the reaction.
- The molecules at which enzymes act are called **substrates**, and enzyme converts them into different molecules, called **products**.

## Quick Quiz-3 (2): How does enzyme work?

## HOW DOES ENZYME WORK?

- When enzyme attaches with substrate, a temporary enzyme-substrate (ES) complex is formed.
- Enzyme catalyzes the reactions and substrate is transformed into product.
- After it, the ES complex breaks enzyme product.



## (A) LOCK AND KEY MODEL:

- In 1894, a German chemist, Emil Fischer proposed lock and key model.
- According to this model, both enzyme and substrate possess specific shapes that fit exactly into one another. This model explains enzyme specificity.

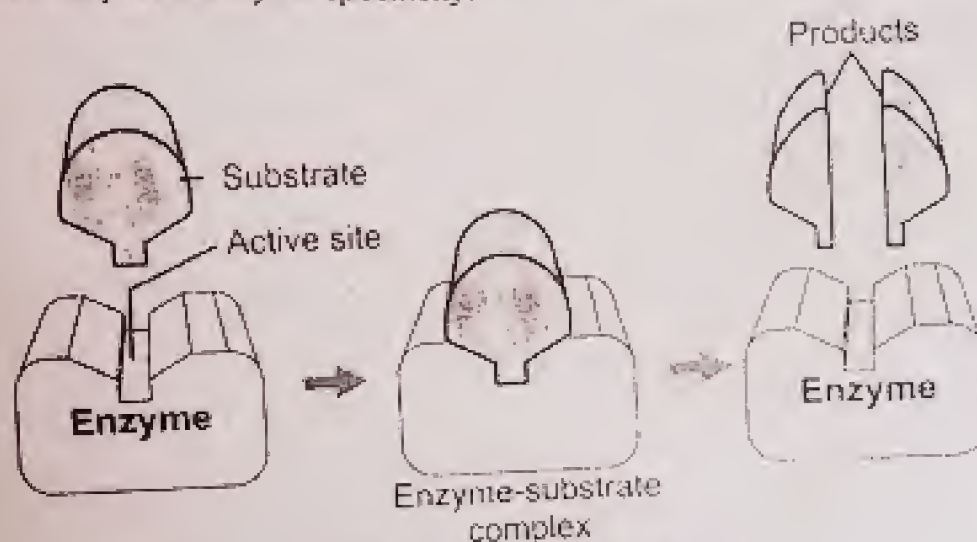
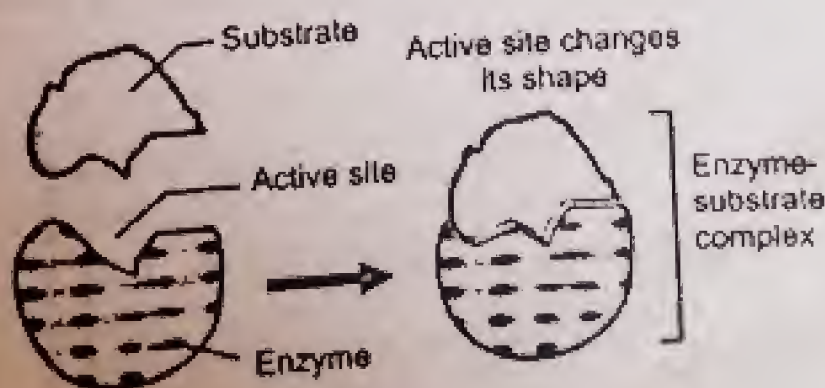


Fig. Lock and Key Model

## (B) INDUCED-FIT MODEL:

- In 1958, an American biologist **Daniel Koshland** suggested a modification to lock and key model and proposed **induced-fit model**.
- According to this model, active site is not a rigid structure. Instead is molded into the required shape to perform its function.



Induced Fit Model

"Induced fit model" is more acceptable than "lock and key" model of enzyme action.



## DO YOU KNOW?

- (1) Wilhelm Kuhne (1978) first time used the term enzyme
- (2) There are over 2000 known enzymes, each of which is involved in one specific chemical reaction.
- (3) Enzymes are substrate specific.
  - The enzyme protease (which breaks peptide bonds in proteins) will not work on starch (which is broken down by an enzyme amylase).
  - Similarly lipase enzyme acts on lipids and digests them into fatty acids and glycerol.

## FACTORS AFFECTING ENZYME ACTIVITY:

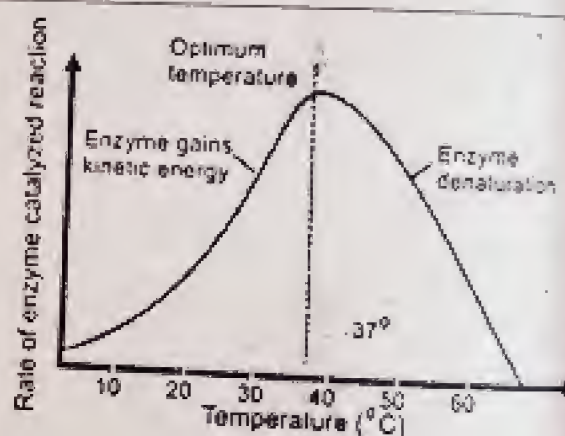
**Exercise Q3 (III):** Briefly describe the factors that affect the Activity of enzymes.

- Enzymes are very sensitive to the environment in which they work.
- Any factor that can change the chemistry or shape of enzyme molecule, can affect its activity.

Following factors affect the enzyme activity

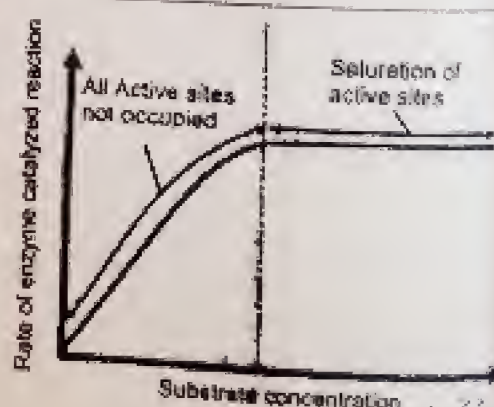
### (i) TEMPERATURE

- Increase in temperature speeds up the rate of enzyme catalyzed reactions, but only to a certain point.
- Every enzyme works at its maximum rate at a specific temperature called as the optimum temperature for that enzyme.
- When temperature rises to a certain limit, heat adds in the activation energy and also provides kinetic energy for the reaction. So reactions are accelerated.
- However, when temperature is raised well above the optimum temperature, heat energy increases the vibrations of atoms of enzyme. Thus, the globular structure of enzyme is lost. This is known as the denaturation of enzyme. It results in a rapid decrease in rate of enzyme action and it may be blocked completely.



### (ii) SUBSTRATE CONCENTRATION

- If enzyme molecules are available in a reaction then increase in substrate concentration increases the rate of reaction.
- If enzyme concentration is kept constant and amount of substrate is increased then a point is reached where further increase in substrate concentration does not increase the rate of reaction. At this point the active sites of all enzymes are occupied at high substrate concentration. Thus, more substrate molecules do not find free active site. This state is called saturation of active site and reaction rate does not increase.



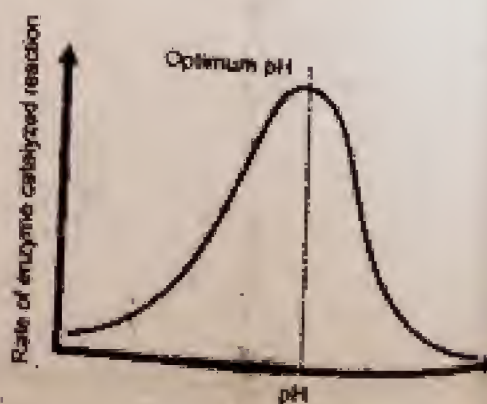
### (iii) pH

- All enzymes work at their maximum rate at a narrow range of pH, called as the optimum pH.
- A slight change in this pH causes retardation in enzyme Activity or blocks it completely.
- Change in pH can affect the ionization of the amino acids at the active site.
- Every enzyme has its specific optimum pH value.

e.g.

pepsin (working in stomach) is active in acidic medium (low pH)

trypsin (working in small intestine) shows its Activity in alkaline medium (high pH).





## ROLE OF INHIBITORS IN ENZYME CATALYZED REACTIONS:

### INHIBITORS:

Substances that tend to decrease the activity of enzymes are called inhibitors.

OR

An inhibitor is a chemical substance which can react (in place of substance) with the enzyme but is never transferred into products by blocking the active site of enzyme temporarily or permanently.

### Examples:

Poisons like cyanide, antibodies, anti-metabolites and some drugs.

### TYPES OF INHIBITORS

Inhibitors can be divided into two types

- Irreversible inhibitors
- Reversible inhibitors

#### Irreversible Inhibitors

- They occupy the active sites by forming covalent bond or they may physically block the active sites.
- They decrease the reaction rate by occupying the active sites or destroying the globular structure of enzymes.

#### Reversible Inhibitors

- They form weak linkages with the enzyme.
- Their effect can be neutralized completely or partly by an increase in the concentration of the substrate.

### ROLE OF INHIBITORS

- The inhibitors may decrease the activity of enzymes and thus the rate of the reaction. It decreases the rate either by combining directly with the enzyme or by reacting with the activator, so that the activator does not remain available to enzyme for activation.

There are two types of inhibitions

#### Competitive Inhibition:

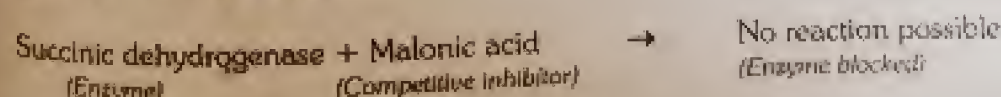
A number of inhibitors have structures similar to substrate molecules. So, due to the structural similarity with the substrate, they may be selected by the enzyme binding sites. However, these are not able to activate the catalytic site. They compete with the original substrate for the same binding site. Often their affinity to the enzyme is much higher than that of the substrate, so the substrate is displaced effectively. The enzyme molecules are thus to a large degree inactivated by the binding of the inhibitors. No products are formed in this way. This type of inhibition is known as "competitive inhibition".

#### Example

Succinic acid (substrate) is converted into Fumaric acid (product) by the enzyme succinic dehydrogenase.



But in the presence of malonic acid (competitive inhibitor) having structural similarity with succinic acid (substrate), the binding sites are occupied by the malonic acid. Hence, no catalysis takes place at the active or catalytic site, hence no product is formed





### Non-Competative Inhibition:

- Another type of inhibitors, called non-competitive inhibitors cause "non competitive inhibition".
- Here, the inhibitor is not bound to the catalytic or active site but to some other site of enzyme. This binding distorts the enzyme's structure also affecting the catalytic site of the enzyme in such a way that even if genuine substrate binds the active sites, catalysis fails to take place.
- In the reactions catalysed by enzymes irreversible inhibitors cause irreversible inhibition either by physically blocking the active sites of enzymes or by occupying the active sites and forming covalent bonds. So the rate of reaction is retarded due to the occupation of active sites of enzymes by irreversible inhibitors or due to destruction of the globular structure of enzymes.

#### Note:

Competitive and non-competitive inhibitors are the two major types of reversible inhibitors.

### INDUSTRIAL APPLICATION OF ENZYME:

Enzymes are extensively used in different industries for fast chemical reactions. For example:

- (1) **Food Industry:** Enzymes that break starch into simple sugars are used in the production of white bread buns etc.
- (2) **Brewing Industry:** Enzymes break starch and proteins. The products are used by yeast for fermentation (to produce alcohol).
- (3) **Paper Industry:** Enzymes break starch to lower its viscosity that aids in making paper.
- (4) **Biological detergent:** Protease enzymes are used for the removal of protein stains from clothes. Amylase enzymes are used in dish washing to remove resistant starch residues.

### QUICK QUIZ-3

- (1) What are enzymes? Why are they called biocatalysts?

Enzymes are biocatalysts which alter the speed of metabolic activities in the living bodies.

Enzymes act as **biocatalysts** because they speed up and regulate metabolic pathways in the living bodies.

- (2) How does enzyme work?  
Page

- (3) Who has used the term Enzyme first time?

Winhelm Kuhne (1978) first time used the term enzyme (Greek: En, in + Zyme, yeast)

- (4) Why are following scientists famous for?

(i) **Emil Fischer**

In 1894, a German chemist, Emil Fischer proposed lock and key model for the working of enzymes. According to this model, both enzyme and substrate possess specific shapes that fit exactly into one another. This model explains enzyme specificity.

(ii) **Daniel Koshland**

In 1958, an American biologist Daniel Koshland proposed the induced-fit model for the working of enzymes. According to this model, active site is not a rigid structure. Instead it is molded into the required shape to perform its function.

- (5) Enzymes are extensively used in different industries. Comment on this statement.

Enzymes are extensively used in different industries for fast chemical reactions. For example:

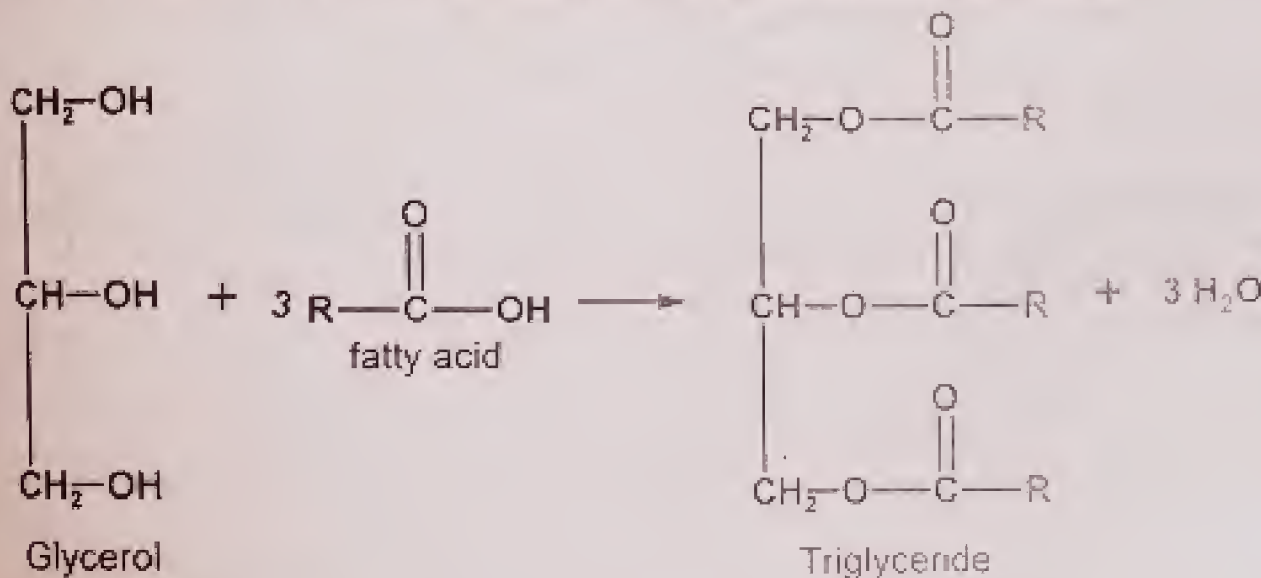
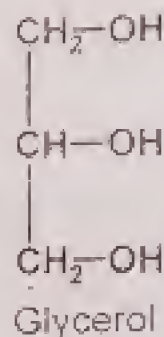
- (i) **Food Industry:** Enzymes that break starch into simple sugars are used in the production of white bread buns etc.
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- (iv) **Biological detergent:** Protease enzymes are used for the removal of protein stains from clothes. Amylase enzymes are used in dish washing to remove resistant starch residues.



## LIPIDS:

Naturally occurring organic compounds of animals and plants origin, which are soluble in organic solvents called lipids.

- The word lipid is derived from Greek word, lipos means fat.
- These molecules consist of carbon, hydrogen, and oxygen atoms.
- The main constituents of all membranes in all cells (cell walls), food storage molecules, intermediaries in signaling pathways, Vitamins A, D, E and K, cholesterol.
- All lipids are hydrophobic:** this is the one property they have in common. This group of molecules includes fats and oils, waxes, phospholipids, steroids (like cholesterol), and some other related compounds.
- Fats and oils are made from two kinds of molecules:** glycerol (a type of alcohol with a hydroxyl group on each of its three carbons) and three fatty acids joined by dehydration synthesis. Since there are three fatty acids attached, these are known as triglycerides.



## CLASSIFICATION OF LIPIDS

There are three broad classes of lipids.

### SIMPLE LIPIDS

These are the ester of fatty acids with glycerol

Examples:

**Triglycerides, neutral fats:** These are found in adipose tissue, butterfat, fish oils, olive oil, and corn oil.

**Waxes:** beeswax, head oil of sperm whale, carnauba oil, and lanolin of industrial and medicinal importance.

### COMPOUND LIPIDS

These contain radicals in addition to fatty acids and alcohols.

Examples:

- Phospholipids (phosphatides):** Found chiefly in animal tissues.
- Plasmalogen:** Found in brain, heart, and muscle.
- Lipositol:** Found in brain, heart, kidneys, and plant tissues together with phytic acid. Phosphatidyl inositol, phosphatide linked to inositol; rapid synthesis and degradation in brain; evidence for role in cell transport processes.
- Sphingomyelin:** Found in nervous tissue, brain, and red blood cells. Source of phosphoric acid in brain tissue.

### DERIVED LIPIDS

These are hydrolytic product of compound lipids.

**Fatty acids:** occur in plant and animal foods; also exhibit in complex forms with other substances. Obtained from hydrolysis of fats; usually contains an even number of carbon atoms and are straight chain derivatives.



**Quick Quiz-4 (3):** Explain briefly the structure of lipids.

## STRUCTURE OF LIPIDS

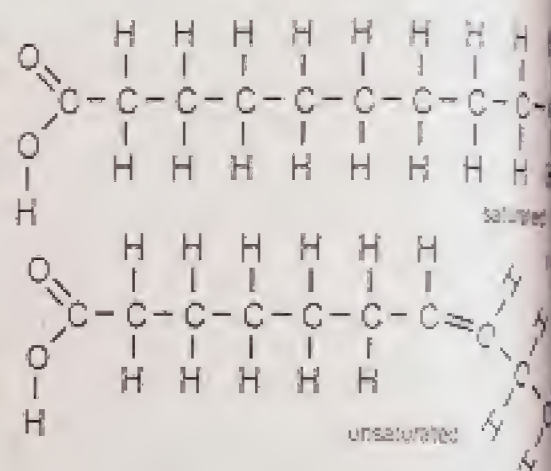
- Lipids are generally defined in terms of solubility, and not in terms of particular structures. In cases of proteins and nucleic acids are defined in terms of particular structures.
- Lipids associate with one another via van der Waals forces and the hydrophobic effect.

### Structure of Fatty Acids

- The "tail" of a fatty acid is a long hydrocarbon chain, making it hydrophobic.
- The "head" of the molecule is a carboxyl group which is hydrophilic.

**Fatty acids are the main components of soap:** In soap their tails are soluble in oily dirt and their heads are in water to emulsify and wash away the oily dirt. However, when the head end is attached to glycerol to form that whole molecule is hydrophobic.

- The terms saturated, mono-unsaturated, and poly-unsaturated shows the number of hydrogens attached to the hydrocarbon tails of the fatty acids as compared to the number of double bonds between carbon atoms in the tail.



### FATS:

- Fats are mostly obtained from animal sources.
- These have all single bonds between the carbons in their fatty acid tails. Thus all the carbons are also bonded to the maximum number of hydrogens possible. Thus, these are called **saturated** fats.
- Fats are solid at room temperature:** It is because the hydrocarbon chains in these fatty acids are fairly straight and can pack closely together. Thus, their melting points are high making these fats solid at room temperature.

### OILS:

- Oils are mostly obtained from plant sources. These, have some double bonds between some of the carbons in the hydrocarbon tail. It causes bends or "kinks" in the shape of the molecules.
- Since, some of the carbon atoms share double bonds so they are bonded to less number of hydrogen atoms than saturated carbon atoms. Therefore these oils are called **unsaturated** fats.
- Oils are liquid at room temperature:** These are liquid at room temperature. It is because of the kinks in the hydrocarbon tails, unsaturated fats cannot pack as closely together. Thus their melting points are low making them liquid at room temperature.

### Important!

The unsaturated fats are "healthier" than the saturated ones.

## PROPERTIES OF LIPIDS

### (1) PHYSICAL PROPERTIES

- (1) Oils and fats may be either liquids or non-crystalline solids at room temperature.
- (2) Fats and oils in the pure states are colorless, odorless and tasteless.
- (3) The color of fats arises due to foreign substances, for example yellow color of the butter is due to the presence of carotene.
- (4) They are lighter than water.
- (5) They are insoluble in water.
- (6) They are readily soluble in organic solvents like diethyl ether, carbon disulphide, acetone, benzene, chloroform and carbon tetrachloride.
- (7) They form emulsions when they are agitated with water in the presence of soap or other emulsifier.
- (8) Fats and oils are poor conductors of heat and electricity and serve as excellent insulators for the animal body.



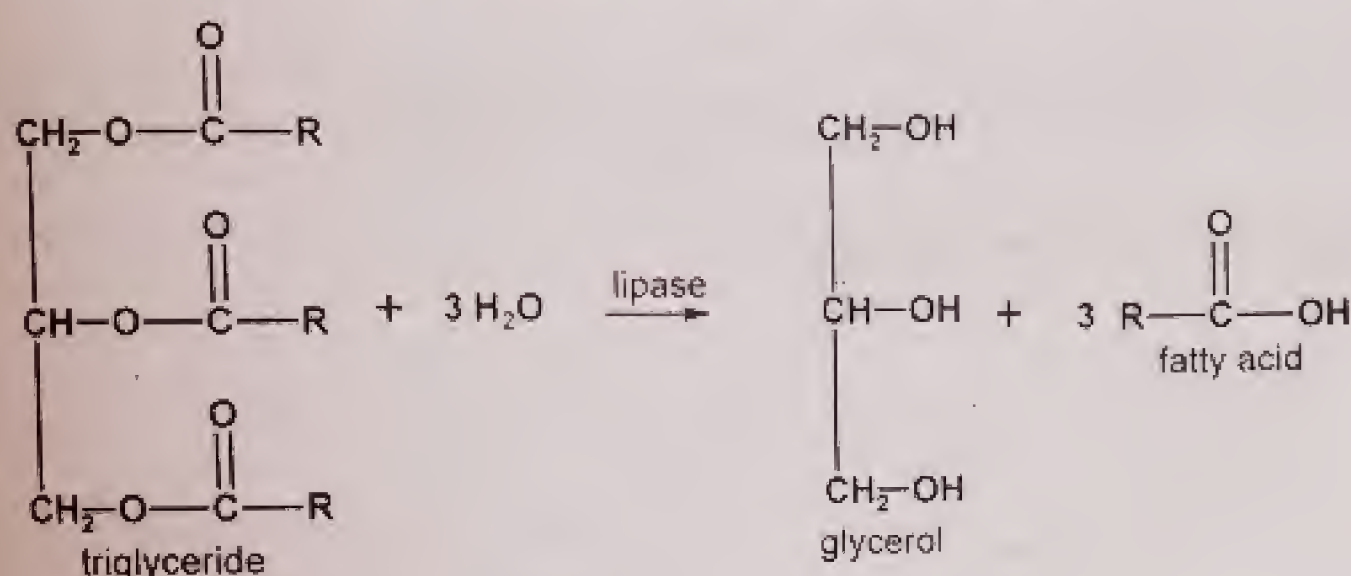
## 2) CHEMICAL PROPERTIES

Fats and oils undergo various types of reaction but the most important are:

- (i) Hydrolysis
- (ii) Hydrogenation

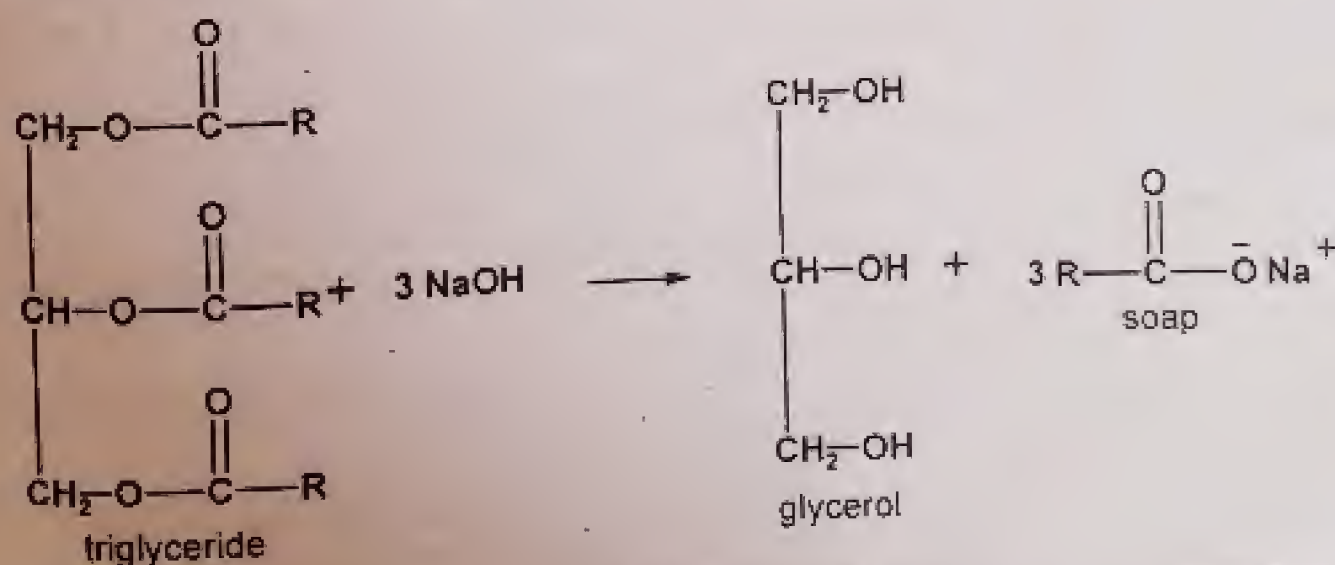
### (i) HYDROLYSIS OF FATS AND OILS

- Fats and oils are triglycerides. They are Triesters. They are hydrolyzed by enzymes which act as catalysts. These enzymes are called lipases.
- Actually this hydrolysis takes place in the digestive tract of human beings and animals. Fatty acids are produced in animal body which play an important role in the metabolic pathways.



### (ii) SAPONIFICATION

- Saponification is the hydrolysis of triglycerides by alkalis.
- Glycerol is produced along with sodium or potassium salt of fatty acids. These sodium and potassium salts are called soaps.

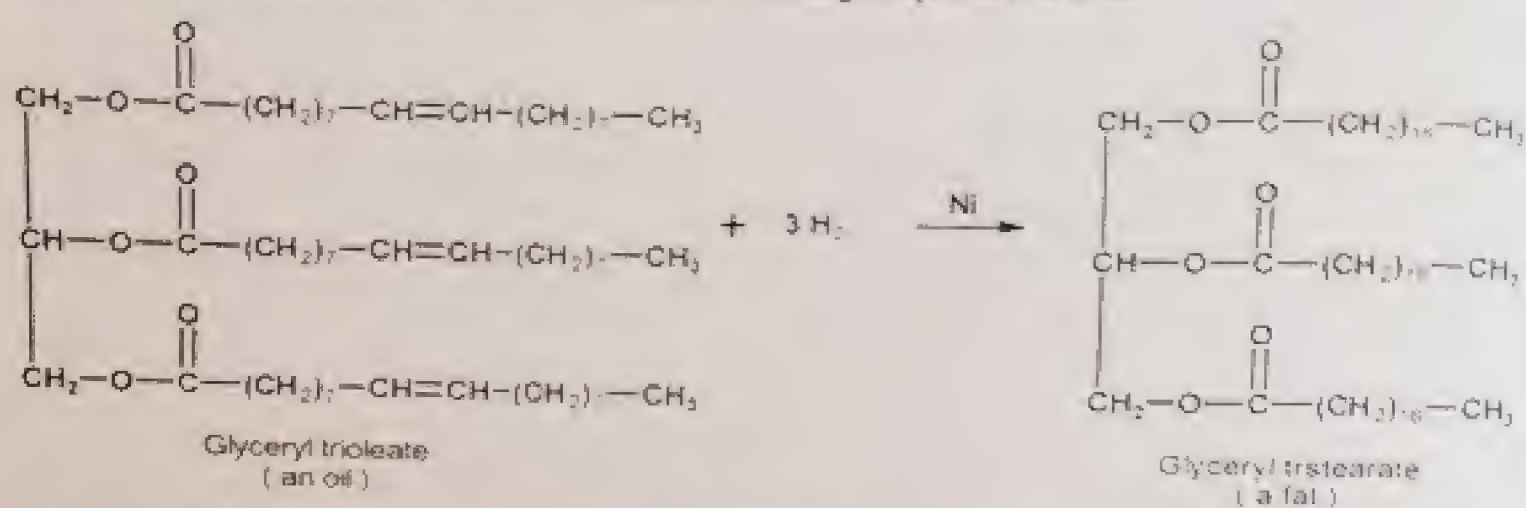


### (iii) HARDENING OF OILS

- The unsaturated triglycerides are liquids at room temperature. They are called oils.
- They can be saturated by passing hydrogen in them in the presence of metal catalysts. So, the liquid triglycerides are converted into a semisolid triglyceride.



- This reaction is used commercially to harden the vegetable oil, for the production of vegetable ghee or margarine.
- These hardened oils are also used extensively for making soaps and candles.



**Exercise Q3 (iv): What is the nutritional importance of Lipids?**

### NUTRITIONAL IMPORTANCE OF LIPIDS

- Lipids play three major biochemical roles:
  - (i) As a storage form for metabolic energy (triglycerides)
  - (ii) As components of membranes
  - (iii) As messengers (prostaglandins, steroid hormones)
- A major role of lipids in nutrition is to provide energy.
- Since unsaturated, saturated and trans fats all provide about 9 calories per g compared to carbohydrates or protein with 4 calories per g.
- Even though it is high in calories, fat does not necessarily cause weight gain if total lipid intake is monitored.
- Our body also needs fat from your diet to be able to absorb and use fat-soluble essential nutrients such as vitamin A, vitamin D and vitamin E.

### ESSENTIAL LIPIDS

- Some nutrients are essential in diet for good health. These are not prepared in body.
- The essential lipids are polyunsaturated fats called omega-6 and omega-3 fats. These fats are needed for hormone synthesis, cell membrane structure and healthy brain and vision. They may help lower blood cholesterol levels.
- The omega-6 fatty acids can be obtained from vegetable oils and nuts.
- Omega-3 fatty acids are also in flaxseed, walnuts and fatty fish.

### NON-ESSENTIAL LIPIDS

- Monounsaturated fatty acids are not essential in the diet because our body can synthesize them.
- They may help reduce risk for heart disease.
- They are in olive oil, peanuts and avocados.
- You do not need to get saturated fat, trans fat or cholesterol in your diet, and these lipids raise bad cholesterol levels in your blood.
- Saturated fat is in fatty meats and cheese, palm and coconut oil, and butter.
- Trans fat is in partially hydrogenated oils in processed and fried foods, while cholesterol is fatty animal foods.

### Information

Our bodies make about 2 g of cholesterol per day, and that makes up about 85% of blood cholesterol, while only about 15% comes from dietary sources.



## FUNCTIONS OF LIPIDS

Some other functions of lipids are:

- tissues reconstruction;
- nervous system organization;
- increases and assures a normal function of the skin;
- antibodies formation;
- good function of endocrine glands(thyroid);
- water metabolism;

## QUICK QUIZ-4

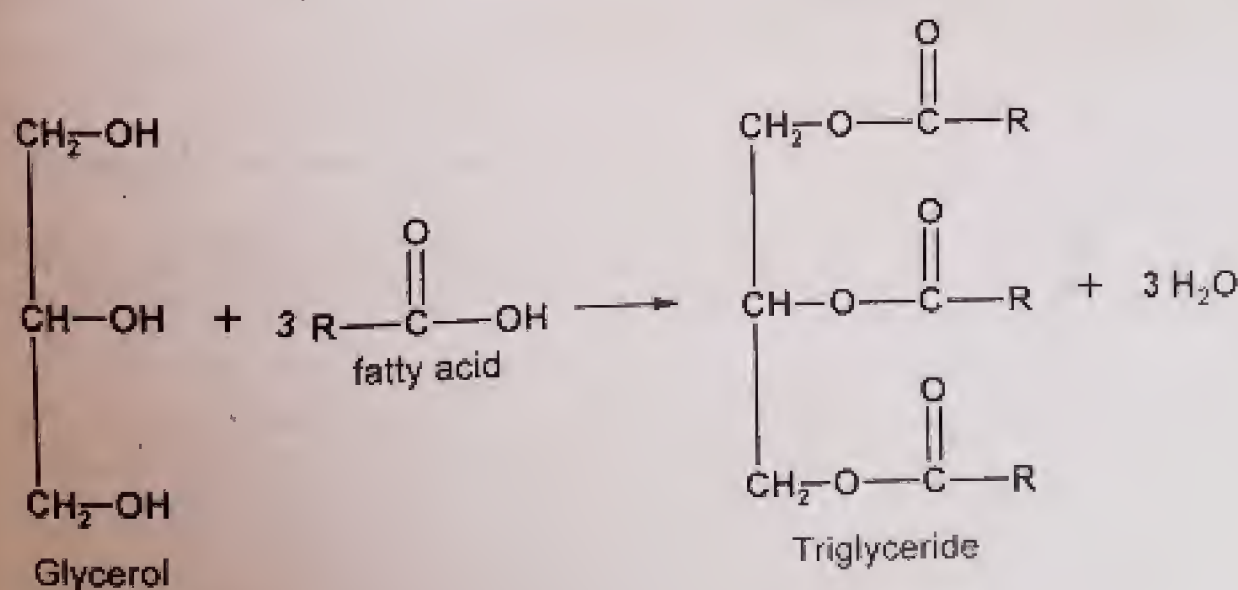
What are lipids? Shortly explain the only property that all the lipids have in common.

Naturally occurring organic compounds of animals and plants origin, which are soluble in organic solvents are called lipids.

All lipids are hydrophobic: This is the one property they have in common. This group of molecules includes fats and oils, waxes, phospholipids, steroids (like cholesterol), and some other related compounds.

2) What are triglycerides? Draw its structure

Fats and oils are made from two kinds of molecules: glycerol and three fatty acids joined by dehydration synthesis. Since there are three fatty acids attached, these are known as triglycerides.



3) Explain briefly the structure of lipids.



## NUCLEIC ACIDS

### Discovery:

- (1) Nucleic acids were first of all demonstrated in the nuclei of puss cells in 1868
- (2) They were found in sperm heads by Friedreich Miescher in 1872.

### Nucleic acids are present in:

- (1) In every living cell as well as in viruses.
- (2) They have been found to be essential substance of genes.

### Properties:

- (1) Nucleic acids contain in their structures the blue-prints for the normal growth and development of every living organism.
- (2) They have two fundamental properties which are common to all living organism.
  - a) The ability to reproduce, store and transmit genetic information
  - b) To undergo mutation.

### Types of Nucleic Acids:

There are two types of nucleic acids which have been discovered:

- (1) Deoxyribonucleic acids (DNA)
- (2) Ribonucleic acid (RNA)

### Nucleic acids and proteins:

- In the human body the nucleic acids occur as part of the conjugated proteins which are called nucleoproteins.
- The nucleic acids direct the synthesis of proteins.

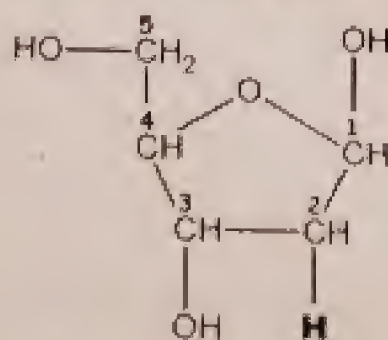
**Exercise Q3 (v):** Explain the structures of Nucleic acids.

### STRUCTURAL COMPONENTS OF DNA AND RNA

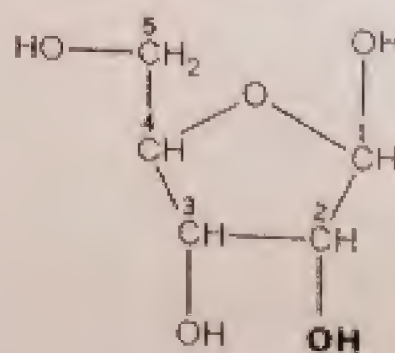
- DNA stands for deoxyribonucleic acid. It is a polymer of deoxyribonucleotides.
- RNA stands for ribonucleic acid. It is a polymer of ribonucleotides.
- The nucleotide consists of: one sugar, one nitrogenous base, and at least one phosphate.
- The structures of all components are given below.

#### (i) SUGAR

- The sugar in DNA is deoxyribose.
- The sugar in RNA is ribose.
- The deoxy- prefix indicates that this form of the sugar contains one less oxygen atom. The C-2 atom of pentose sugar has two hydrogens attached to it instead of a hydrogen and hydroxyl (-OH).



Deoxyribose sugar



Ribose

- All of the nitrogenous bases are linked to the C-1 atom of the sugar by removing OH group.
- The phosphate group is attached to the hydroxyl group of C-5 atom.

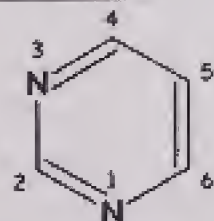


## NITROGENOUS BASES

### Quick Quiz-5 (2): Differentiate purines and pyrimidines.

#### Pyrimidines

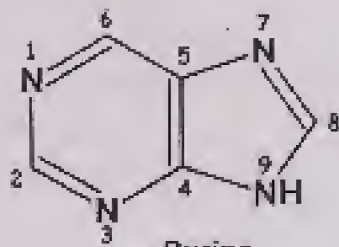
- There are three pyrimidine bases.
- Each consists of a 6-membered ring containing both nitrogen and carbon atoms.
- Two pyrimidines, Thymine and Cytosine, are found in DNA.
- RNA also contains two pyrimidines, but they are Cytosine and Uracil.



Pyrimidine

#### Purines

- The purines are made from two heterocyclic rings of carbon and nitrogen.
- In purines a 6-member and a 5-member ring are fused.
- There are two purines, Adenine and Guanine.
- These are found in both DNA and RNA.



Purine

## PHOSPHATES

- The addition of one or more phosphate groups to a nucleoside, makes it a nucleotide.
- The nucleotide consists of a base-sugar-phosphate unit.
- These units on polymerization forms DNA.

### Difference between DNA and RNA

They differ in following ways.

- 1) The sugar in RNA is ribose while the sugar in DNA is 2-deoxyribose.
- 2) Four different bases are found in DNA cytosine (C) thiamine (T) adenine (A) and guanine (G). In RNA thiamine does not occur and its place is taken by uracil (U).
- 3) DNA is nearly always double stranded, while RNA is usually single strand.
- 4) DNA is used to store information while RNA is used to transfer information.

## QUICK QUIZ-5

### 1) Write the names of structural components of DNA and RNA

Both DNA and RNA are polymers of nucleotides.

The nucleotide consists of: one sugar, one nitrogenous base, and at least one phosphate.

**Sugar:** In DNA; it is deoxyribose sugar and in RNA it is ribose sugar.

**Nitrogen bases:** In DNA, four nitrogenous bases are: Adenine, Guanine, Cytosine and Thiamine

In RNA, four nitrogenous bases are: Adenine, Guanine, Cytosine and Uracil

**Phosphate:** The phosphate is similar in both DNA and RNA.

### 2) Differentiate purines and pyrimidines.

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### 3) Which purines are present both in DNA and RNA?

Two purines are present in both DNA and RNA: Adenine(A) and Guanine(G).



## MINERALS OF BIOLOGICAL SIGNIFICANCE

- Minerals are the nutrients that exist in the body.
- These are as essential as our need for oxygen to sustain life.
- Minerals are also found in organic and inorganic combinations in food.
- In the body only 5% of the human body weight is mineral matter, vital to all mental & physical processes for total well being.
- They are most important factors in maintaining all physiological processes, are constituents of the bones, tissues, blood, muscle, and nerve cells.
- Many of them act as catalysts for many biological reactions within the human body.
- They are necessary for transmission of messages through the nervous system, digestion, & metabolism utilization of all nutrients in foods.
- Vitamins cannot be properly assimilated without the correct balance of minerals. e.g. calcium is needed for vitamin "C" utilization, zinc for vitamin "A", magnesium for "B" complex vitamins, selenium for vitamin "E" absorption, etc.

### Important minerals in human diet and their roles

Human diet and their roles		
Minerals	Role in body	
Major minerals		
Sodium	Fluid balance in the body Helps in absorption of other nutrients	Important for muscle contraction, nerve impulse transmission, heart function, and blood pressure
Potassium	Fluid balance in the body Acts as cofactor for enzymes	
Chloride	Fluid balance in the body Component of hydrochloric acid	
Calcium	Development and maintenance of bones and teeth and Blood clotting	
Magnesium & Phosphorus	Development and maintenance of bones and teeth	
Trace Minerals		
Iron	Oxygen transport and storage	Act as enzyme cofactors Support immune function
Zinc	Aids insulin action Helps in growth and reproduction	
Copper	Acts as enzyme cofactor	
Chromium	Helps in insulin action	
Fluoride	Stabilizes bone mineral and hardens tooth enamel	
Iodine	Essential for normal thyroid function	



## SOURCES OF IMPORTANT MINERALS

Exercise Q3 (vi): Describe four important minerals and their sources.

### CALCIUM

Calcium is important to bone growth and formation, blood clotting and nerve and muscle functioning.

#### Sources:

Calcium is obtained from milk, cheese, egg yolk, beans, nuts, cabbage etc.

#### Deficiency:

A deficiency may result in arm and leg muscles spasms, softening of bones, back and leg cramps, brittle bones, rickets, poor growth, osteoporosis, tooth decay and mental depression.

### IRON

- Iron is an essential mineral.
- Its major function is to combine with protein and copper in making hemoglobin. The hemoglobin is present in the blood and carries oxygen from the lungs to the tissues throughout the body.

#### Sources:

Iron is obtained from red meat, egg yolk, whole wheat, fish, spinach and mustard etc.

#### Deficiency:

A deficiency may result in weakness, fatigue, pale skin, constipation and anemia.

### PHOSPHORUS

- Phosphorus is after calcium the second most abundant mineral in the body.
- It is a principal mineral of bones and teeth.
- It is involved in most metabolic actions in the body, including kidney functioning, cell growth and the contraction of the heart muscle.

Sources: Phosphorus is obtained from egg yolk, cheese, milk, cabbage etc.

Deficiency: A deficiency is unusual, but may have symptoms varying from painful bones, irregular breathing, fatigue, anxiety, numbness, skin sensitivity and changes in body weight.

### ZINC

- Zinc is vital to immune resistance, wound healing, digestion, reproduction, physical growth, diabetes control, taste and smell and maintaining normal Vitamin A levels and usage.
- Zinc can be found in almost every cell of the body and serves as part of more than 70 enzymes that control body processes.

Sources: We get zinc from Oyster, red meat, chicken, beans, nuts, dairy products and some sea foods.

Deficiency: A deficiency may result in poor growth, acne-like rash, hair loss, diarrhea, delayed sexual maturation, impotence, sterility, eye lesions, loss of appetite, reduced sense of taste and smell, skin lesions and inflammation, poor wound healing, reduced resistance to infections, mental confusion, poor learning ability, changes in hair and nails and anemia.



## BIOLOGICAL SIGNIFICANCE OF MINERALS

### (A) IMPORTANCE/SIGNIFICANCE OF IRON

The primary role of iron relates to the ability of red blood cells to carry oxygen for use throughout the entire body. Some functions of iron are mentioned below.

#### Fatigue

- To prevent fatigue, iron is needed by the body to make hemoglobin rich blood which transports oxygen to the cells.
- It is also needed for adenosine triphosphate production (ATP), which is essential for cellular energy and proper cell function.

#### Exercise

- Iron is lost through sweat and through bleeding of the digestive tract from the harsh motion of exercise.
- Studies indicate that 34% of female runners and 8% male runners are iron deficient.

#### Pregnancy

- Iron is needed for proper placenta development.
- It is also needed for the prevention of pre-term and low birth weight babies.
- Studies estimate that up to 58% of pregnant women are iron deficient.

#### Pediatric

- Iron is essential during the first eight months for brain growth.
- The effects of anemia may be associated with developmental delays in both motor and cognitive abilities.

#### Treatment Duration

- Up to six months to restore low iron stores, its sufficient quantity must be used.
- When iron deficiency is left untreated, it can lead to conditions that are more serious.

#### Metabolic Processes

- Iron plays an important part in the metabolic processes of the animals.
- The function of iron in the body is limited almost exclusively to the oxygen transport in the blood, through hemoglobin.
- It is present in some enzymes that catalyze reactions of cellular oxidation.
- In human body, the richest organs in iron are liver and spleen.
- In smaller amount, it is also present in bones, medulla, kidneys and intestines.

### (B) IMPORTANCE/SIGNIFICANCE OF CALCIUM:

#### Occurrence In Human:

- Calcium is the most common mineral in the human body.
- It is present in the body in almost the same relative abundance as in the earth's crust.
- There are six stable isotopes of calcium. calcium-40 is the most common (97 %), and calcium-46 is the least abundant (0.003 %).

#### Importance:

- The integrity of the system depends critically on vitamin D status. If there is a deficiency of vitamin D, the loss of its calcaemic action leads to a decrease in the ionised calcium and secondary hyperparathyroidism and hypophosphataemia. This is why experimental vitamin D deficiency results in rickets and osteomalacia whereas calcium deficiency gives rise to osteoporosis.
- Approximately 99% of total body calcium is in the skeleton and teeth and 1% in blood and soft tissues.
- Calcium has four major biological functions:
  - (i) Structural as stores in the skeleton
  - (ii) Electrophysiological - carries charge during an action potential across membranes
  - (iii) Intracellular regulator, and



(iv) As a cofactor for extracellular enzymes and regulatory proteins

### IMPORTANCE/SIGNIFICANCE OF PHOSPHORUS

#### Occurrence in Human:

- Phosphorus is present in plants and animals
- There is over 1 lb (454 grams) of phosphorus in the human body
- It is a component of adenosine triphosphate (ATP), a fundamental energy source in living things
- It is found in complex organic compounds in the blood, muscles and nerves, and in calcium phosphate. The calcium phosphate is the principal material in bones and teeth
- Phosphorus compounds are essential in the diet. Organic phosphates, ferric phosphate, and monocalcium phosphate are added to foods. Dicalcium phosphate is added to animal feeds.

#### Importance:

- The main function of phosphorus is in the formation of bones and teeth
- It plays an important role in the body's utilization of carbohydrates and fats and in the synthesis of protein for the growth, maintenance, and repair of cells and tissues
- It is also crucial for the production of ATP, a molecule the body uses to store energy
- Phosphorus works with the B vitamins
- It also assists in the contraction of muscles, in the functioning of kidneys, in maintaining the regularity of the heartbeat, and in nerve conduction

### IMPORTANCE/SIGNIFICANCE OF ZINC

- Zinc is the most omnipresent of all trace elements involved in human metabolism
- More than a hundred specific enzymes require zinc for their catalytic function.
- If zinc is removed from the catalytic site, Activity is lost. However, the replacement of zinc restores Activity.
- Studies in individuals with acrodermatitis enteropathica showed the functional outcomes of zinc deficiency. These include impairments of dermal, gastrointestinal, neurologic and immunologic systems.
- Acrodermatitis enteropathica a genetic disorder with zinc malabsorption resulting in severe deficiency.
- Loss of zinc through gastrointestinal tract accounts for approximately half of all zinc eliminated from the body.
- Considerable amount of zinc is secreted through the biliary and intestinal secretions, but most of it is reabsorbed and this process is an important point of regulation of zinc balance.
- Other routes of zinc excretion include the urine and surface losses (desquamated skin, hair, sweat).

## SOCIETY, TECHNOLOGY AND SCIENCE

#### Glycogen - A store house

Glycogen is reserved food material that store in muscles and liver in animals and human. When body requires energy due to lack of glucose, the glycogen reconverted into glucose and provide energy to the body in the form of ATP.

#### Hibernating Animals and Reserve Food

Large amount of fat is store in the body of some animals that hibernate during winter. In winter the metabolic activities slow down. They use this fat as reserved food material that produce ATP during oxidation.

### COMPLEX CARBOHYDRATES WHICH PROVIDE LUBRICATION TO THE ELBOW AND KNEE:

- Glucosamine, glucosaminoglycons or proteoglycan are the complex carbohydrates which provide lubrication to elbow and knee.
- Glucosamine ( $C_6H_{13}NO_5$ ) is an amino sugar. It is produced naturally in the body and plays a key role in building cartilage and lubricating joints. It is found in the fluid that is around joints. It is a prominent precursor for glycosaminoglycans and for glycosylated proteins and lipids.
- Glucosamine has been shown to help keep our joints resilient and healthy by lubricating and resting the connective tissue. It is a naturally occurring nutrient and is a glutamine derivative that retains an amine group and a sugar molecule (glucose).



- Over time, every day wear and tear, less than perfect nutrition, injuries and aging can result in dry, brittle cartilage which is vulnerable to damage and stiffening. Research has shown that glucosamine may help repair damaged or strained connective tissue.
- Our joints are made up of two third of water yet are into able to attract and retain it. Glucosamine is shown to help keep cartilage resilient and healthy by attracting and holding water and nutrients within the matrix. Studies have even shown glucosamine may even help to regenerate new cartilage once it becomes damaged, thereby restoring joint function and mobility. Because of its ability to help to lubricate and repair elbow and knee joints, it is quite popular with weight trainers, sports enthusiasts etc.

### GLUCOSAMINOGLYCANS (GAGs)

These are the most abundant heteropolysaccharides in the body. They are long unbranched molecules containing a repeating disaccharide unit. Usually one sugar is uronic acid and the other is either GlcNAc or GalNAc. GAGs have negative charge on them. GAGs are a major component of joint cartilage.

- **Chondroitin sulphate** (D. glucuronate + GalNAc sulphate) is the most abundant GAG found in cartilage. Keratan sulphate (Gal + GlcNAc sulphate) is often aggregated with chondroitin sulphate.
- **GAGs** have unique properties i.e. the ability to fill space, bind and retain water and repel negatively charged molecules. Because of high viscosity and low compressibility, they are ideal for a lubricating fluid in the joints especially in knee and elbow. On the other hand, their rigidity provides structural integrity to the cells.
- **Proteoglycans** (mucopolysaccharides) are formed of glycosaminoglycans (GAGs) and core proteins, covalently bonded to each other. These are found in all connective tissues.
- **Proteoglycans** can also be called joint grease. Proteoglycan appears to be a necessary compound in synovial fluid for normal joint lubrication and function. (Synovial fluid is a clear pale yellow fluid, the main function of which is to serve as a lubricant in joints or tendon sheath.)
- **Aggrecan** is one of the most important extra cellular proteoglycan. To each aggrecan core protein, multiple chains of chondroitin sulphate and keratan sulphate are covalently attached through the trisaccharide linkage. They play an important role in hydration of cartilage of joints. They give cartilage its gel like properties and lubricate it and provide resistance to deformation.

### FIBROUS PROTEINS FROM HAIR AND SILK

- Fibrous proteins consist of elongated molecules having one or more polypeptide chains in the form of fibrous structure.
  - Secondary structure is most important in them.
  - They are insoluble in aqueous media, a property due to a high concentration of hydrophobic amino acid residues both in interior of the proteins and on its surface.
  - They are non-crystalline and are elastic in nature.
  - Their characteristic feature is regular repeating pattern.
  - They play structural or supporting role in the body.
- Examples:** are silk fiber, keratin (of nails, and hair), myosin (in muscle cells), fibrin of blood clot.

### INSULIN - A PROTEIN HORMONE WHOSE DEFICIENCY LEADS TO DIABETES MELLITUS.

#### Structure:

- Insulin is a 51 amino acid peptide hormone that is produced exclusively by pancreatic beta cells.
- F. Sanger was the first scientist who determined the sequence of amino acids in insulin.
- After 10 years of careful work, he concluded that insulin is composed up of 51 amino acids in two chains, one alpha chain and one beta chain.
- The alpha chain contains 21 amino acids.
- The beta chain contains 30 amino acids. Both chains are held together by disulphide bridges. Two inter-chain disulphide bridges and one intra-chain disulphide bridge are present in the beta chain.
- The molecule weight of insulin is 5808.



Function:

- Insulin hormone is central in regulating carbohydrate and fat metabolism in the body.
- It causes the cells in liver, muscles and fat tissue to take up glucose from the blood.
- In the liver and skeletal muscles, glucose is stored as glycogen, while in adipocytes, it is stored as triglycerides.
- Insulin stops the use of fat as energy source. When blood glucose level falls below a certain limit, the body begins to use stored sugar as an energy source through glycogenolysis.
- As a central metabolic control mechanism its status is also used as a control signal to other body systems (such as amino acids uptake by body cells.).
- In addition, it has several other anabolic effects throughout the body.
- Insulin is used medicinally to treat some forms of diabetes patients.

### ROLE OF MINERALS IN THE BODY

- Minerals act as cofactors for the enzyme reactions. Enzymes don't work without minerals. All cells require enzymes to work and function. They give us our vitality.
- They maintain the pH balance within the body.
- Minerals actually facilitate the transfer of nutrients across cell membranes.
- They maintain proper nerve conduction.
- Minerals help to contract and relax muscles.
- They help to regulate our bodies' tissue growth.
- Minerals provide structural support for the body.

These are two categories of mineral essential within body, macro-minerals and micro-minerals. There is no one mineral deficiency. They all must be maintained in balance within body.

#### MACRO-MINERALS:

- Calcium
- Chloride
- Phosphorous
- Sodium
- Potassium
- Sulfur
- Magnesium

#### MICRO-MINERALS (OR TRACE MINERALS):

- Iron
- Boron
- Chromium
- Iodine
- Manganese
- Molybdenum
- Selenium
- Silicon
- Copper
- Cobalt
- Rubidium
- Germanium
- Lithium
- Zinc
- Vanadium



### Structure and Function of Minerals

- The term mineral is applied to chemical elements present in the ash of calcined tissue.
- Dietary minerals are present in inorganic salts, or as part of carbon containing organic compounds, e.g., magnesium is present in chlorophyll, the pigment that makes plants green.
- Six minerals are required by people in gram amounts: sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), phosphorus (P), and chloride (Cl).
- Daily requirements range from 0.3 to 2.0 grams per day.
- Nine trace minerals are required by people in minute amounts: chromium (Cr), copper (Cu), iodine (I), iron (Fe), fluoride (F), manganese (Mn), molybdenum (Mo), selenium (Se), and zinc (Zn).
- There are additional requirements for cobalt (Co) but these are generally expressed in terms of the cobalt containing vitamin B<sub>12</sub>. All trace minerals are toxic at high levels.

### CALCIUM

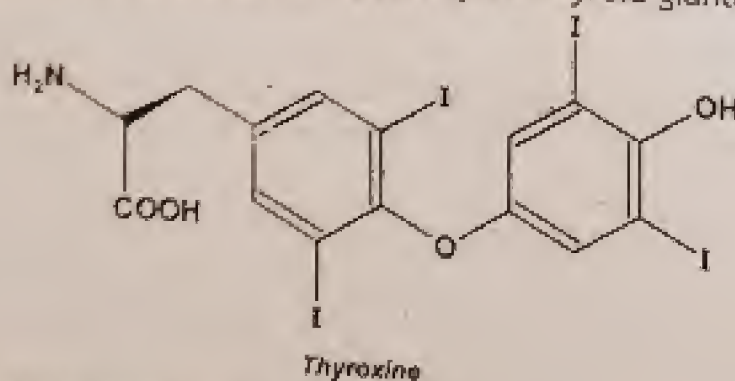
- Calcium is the most abundant mineral in the human body.
- More than 99% of total body calcium is stored in the bones and teeth.
- Calcium is also found in body fluid where its function is to regulate contractions of blood vessels and muscles.
- The requirement for calcium is greatest from puberty to maturity, when the body grows very quickly.
- Milk and dairy products are good sources of calcium.

### FLUORINE

- Most of the body's fluorine (F) is contained in bones and teeth.
- The main source of fluoride is drinking water.
- Fluorine hardens tooth enamel and effectively prevents dental caries.
- Excessive fluorine in drinking water can accumulate in teeth and bones, causing fluorosis.
- Permanent teeth that develop during high fluorine intake have irregularly distributed chalky patches on the surface of the enamel which become stained yellow or brown, producing a characteristic mottled appearance.

### IODINE

- Iodine (I) is primarily involved in the synthesis of two thyroid hormones, thyroxine and triiodothyronine.
- In adults about 80% of the iodide absorbed is trapped by the thyroid gland.

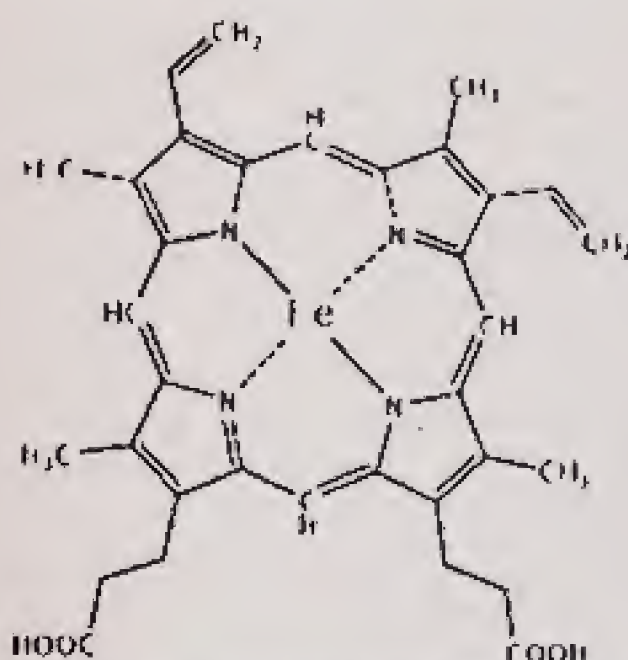


- Most environmental iodine occurs in seawater.
- People living far from the sea are at particular risk of deficiency.
- Salt fortified with iodide (typically 70ug/g) helps ensure adequate intake (100ug/day).
- Deficiency is rare in areas where iodized salt is used but common world wide.
- Iodine deficiency develops when iodide intake is less than 20ug/day.
- In mild or moderate deficiency the thyroid gland hypertrophies to concentrate iodine in itself, resulting goiter which is an enlargement of the thyroid gland visible as a swelling of front the of neck.
- Excessive iodine consumption can lead to thyrotoxicosis, a condition resulting from high concentrations of thyroid hormones in the body which can result from eating foods that have high amounts of iodine, such as kombu-type kelp or seaweed.



IRON

- Iron (Fe) is a component of hemoglobin, myoglobin, and many enzymes in the body.
- Heme iron, contained mainly in animal products is absorbed much better than nonheme iron, which accounts for over 85% of iron in the average diet.
- However, absorption of nonheme iron is increased when it is consumed with animal protein and vitamin C.
- The Recommended Daily Allowance (RDA) of iron is 8 milligrams for men and postmenopausal women.
- Iron deficiency, which may be caused by improper vegan or ovo-lacto vegetarian diets.
- Chronic bleeding may also cause iron deficiency, iron may accumulate in the body when a person is given repeated blood transfusions or takes an overdose of iron supplements.
- Excess iron is toxic any damage the intestines and other organs, as well as cause vomiting and diarrhea.



Heme, a constituent of hemoglobin

## MAGNESIUM

- Magnesium (Mg) has several important metabolic functions in the production and transport of energy.
- It is also important for the contraction and relaxation of muscles.
- Magnesium is involved in the synthesis of protein, and it assists in the functioning of some enzymes.
- Most dietary magnesium comes from nuts, cereals, and dark green, leafy vegetable which are rich in chlorophyll.

## MANGANESE

- Manganese (Mn) is necessary for healthy bone structure and is a component of several enzyme systems including manganese-specific glycosyltransferases and phosphoenolpyruvate carboxykinase.
- Manganese is found in cereal and nuts.
- The adequate intake of manganese is 2 to 5 mg/day.

## MOLYBDENUM

- Molybdenum (Mo) is a component of coenzymes necessary for the activity of xanthine oxidase, sulfite oxidase, and aldehyde oxidase.
- Sulfite oxidase catalyses the transformation of sulfite to sulfate which is necessary for the metabolism of sulfur containing amino acids, such as cysteine.
- Legumes such lentils, beans, and peas are good sources of molybdenum.



## POTASSIUM

- Potassium (K) maintains fluid volume inside and outside of cells, and acts to blunt the rise of blood pressure in response to excess sodium intake.
- The adequate intake of potassium is 4.5 grams per day for children 9 to 13 years old and 4.7 grams per day for older person.
- Potassium is generally found in fruits and vegetables, dried peas, dairy products, meats and nuts.
- Potassium from supplements or salt substitutes can result in hyperkalemia and possibly sudden death if excessively consumed by individuals with chronic renal insufficiency (kidney disease) or diabetes.

## SELENIUM

- Selenium (Se) is a part of the enzyme glutathione peroxidase, which metabolizes hydro-peroxides formed from polyunsaturated fatty acids.
- Selenium is also a part of the enzyme that deiodinate thyroid hormones.
- Generally, selenium acts as an antioxidant that works with vitamin E.
- The deficiency of selenium causes Keshan disease which is a form of congestive cardiomyopathy.
- The RDA for selenium is 70 micrograms (mcg).
- The tolerable upper level of selenium is 400 mcg/day for adults based on the prevention of hair and nail brittleness and early signs of chronic selenium toxicity.

## SODIUM

- Sodium (Na) is usually consumed as table salt (Sodium Chloride, NaCl).
- The adequate intake of 1.5 grams per day with an upper limit of 2.3 grams per day is calculated to meet needs for sweat losses for individuals 8 years or older engaged in recommended levels of physical activity.
- Active people in humid climates who sweat excessively may need more than the adequate intake.

## ZINC

- Zinc (Zn) is contained mainly in bones, teeth, hair, skin, hair, liver, muscle, leukocytes, and testes.
- Zinc is a component of several hundred enzymes, including many nicotinamide adenine dinucleotide (NADH) dehydrogenases, RNA and DNA polymerases, and DNA transcription factors as well as alkaline phosphatase, super oxide dismutase, and carbonic anhydrase.
- Good dietary sources of zinc include mollusks, such as oysters, and cereals.

## KEY POINTS

- Carbohydrates are the most abundant macromolecule on earth. They are of three types i.e. Monosaccharides, disaccharides and polysaccharides.
- People eating a diet high in carbohydrates are less likely to accumulate body fat compared with those who follow a carbohydrate /high-fat diet.
- Proteins are the most important class of biomolecules. They are major structural components of animals and human tissues. They are classified as a simple & protein, conjugated proteins and derived proteins. They are actually polymers of Amino acids.
- Nucleoproteins act as the carrier of heredity from one generation to the other.
- Hemoglobin is a protein and carrier of oxygen. Some of the proteins act as hormones.
- Enzymes are biocatalyst and catalyze chemical reactions in living organisms. They are quite specific in their function. Their Activity depends upon temperature, substrate concentration and pH. They are protein in nature and are used extensively in food, brewing, paper industries.
- All lipids are hydrophobic. Fats are solid while oils are liquid at room temperature. They are insoluble in water but soluble in organic solvents such as diethyl ether, acetone, benzene etc.
- Some lipids are essential for our diet and some are non-essential.
- Nucleic acids are present in every living cell as well as in viruses. They have ability to reproduce, store and transfer genetic information. They are of two types DNA and RNA. Nucleotide is the structural unit of DNA and consists of a sugar, one nitrogenous base and at least one phosphate.
- Minerals are the nutrients and are as necessary as oxygen for life. They are constituents of teeth, bones, tissues, blood, muscles and nerve tissues.
- Minerals are classified as major and trace minerals i.e. those required in appreciable quantity are major and those required in low quantity are trace.



## EXERCISE

Select the right answer from the choices given with each question.

Biochemistry covers the practical applications of:

- (a) Medicine (b) Agriculture (c) Nutrition (d) All of these

Macromolecules are of how many types?

- (a) Three (b) Four (c) Five (d) Six

The general formula for Carbohydrates is:

- (a)  $N_n(H_2O)_n$  (b)  $P_n(H_2O)_n$  (c)  $C_n(H_2O)_n$  (d)  $H_n(CO_2)_n$

Most organic matter on earth is made up of:

- (a) Carbohydrates (b) Lipids (c) Olive Oils (d) Proteins

The no. of Carbon atoms in Hexose is:

- (a) One (b) Four (c) Six (d) Ten

The long chains of Amino Acids are called:

- (a) Oils (b) Polypeptides (c) Proteins (d) Monopeptides

Proteins are used in both forms of:

- (a) Catabolism (b) Anabolism (c) Enzymes (d) Metabolism

What is TRUE about enzymes?

- (a) They make biochemical reaction to proceed spontaneously  
(b) They lower the activation energy of a reaction  
(c) They are not very specific in their choice of substrates  
(d) They are needed in large quantities

To what category of molecules do enzymes belong?

- (a) Carbohydrates (b) Lipids (c) Nucleic acids (d) Proteins

What is TRUE about cofactors?

- (a) Break hydrogen bonds in proteins (b) Help facilitate enzyme Activity  
(c) Increase activation energy (d) Are composed of proteins

Prosthetic groups are:

- (a) Required by all enzyme (b) Loosely attached with enzymes  
(c) Proteinous nature (d) Tightly bound to enzyme

Lipids are generally defined in terms of:

- (a) Solubility (b) Structure (c) Molarity (d) All of these

DNA and RNA are made up of:

- (a) Peptides (b) Nucleotides (c) Neurons (d) None of these

\_\_\_\_\_ of the human body weight is mineral matter?

- (a) 5% (b) 10% (c) 50% (d) 100%

\_\_\_\_\_ is needed for Vitamin C utilization.

- (a) Acid (b) Iron (c) Phosphorus (d) Calcium

The component of blood that carries oxygen in the body is:

- (a) Fats (b) Myoglobin (c) Hemoglobin (d) Amino Acids

Most RNA molecules are:

- (a) Independent (b) Double Stranded (c) Single Stranded (d) Multiple Stranded

\_\_\_\_\_ are the major component of soap.

- (a) Fatty Acids (b) Palm Oils (c) Proteins (d) Saccharides

The mineral, related with the formation of bones and teeth, is:

- (a) RNA (b) Phosphorus (c) Iron (d) Sulphur

## ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (d) All of these

Biochemistry covers medicine, agriculture, nutrition etc.

(ii) Ans: (b) Four

Four main types of macromolecules control all activities. They are carbohydrates, proteins, lipids and nucleic acids

(iv) Ans: (a) Carbohydrates

Most organic matter on earth is made up of carbohydrates

(iii) Ans: (c)  $C_n(H_2O)_n$

The general formula for carbohydrates is  $C_n(H_2O)_n$ . That's why



such compounds were called "hydrates of carbon" mean carbohydrates. e.g. glucose is  $C_6H_{12}O_6$  or  $C_6(H_2O)_6$

because they are involved in many aspects of life

(v) Ans: (c) Six

The no. of Carbon atoms in Hexose is six. e.g. glucose ( $C_6H_{12}O_6$ ) is a hexose as it contains six carbon atoms.

(vii) Ans: (d) Metabolism

Metabolism consists of two types: anabolism and catabolism.

(ix) Ans: (d) Proteins

Enzymes are protein in nature

(xi) Ans: (a) Required by all enzyme

Prosthetic group is co-enzyme. Without this enzyme cannot work. So, they are required by all enzymes

(xiii) Ans: (b) Nucleotides

DNA and RNA are polymers of nucleotides. A nucleotide consists of: one sugar, one nitrogenous base, and at least one phosphate.

(xv) Ans: (d) Calcium

Calcium is needed for vitamin "C" utilization

(xvii) Ans: (c) Single Stranded

RNA molecules are single stranded while DNA molecules are double stranded.

(xvii) Ans: (b) Phosphorus

The main function of phosphorus is in the formation of bones and teeth. The calcium phosphate is the principal material in bones and teeth.

(vi) Ans: (b) Polypeptides

When amino acids are joined together in long chains by peptide bond, then the compound is called polypeptide.

(viii) Ans: (b) They lower the activation energy of a reaction

(x) Ans: (b) Help facilitate enzyme Activity

Co-enzymes are "assistant" of an enzyme. Therefore they facilitate the enzyme activity.

(xii) Ans: (a) Solubility

Lipids are defined as: Naturally occurring organic compounds of animals and plants origin, which are insoluble in organic solvents are called lipids. Thus, they are insoluble.

(xiv) Ans: (a) 5 %

In the body only 5% of the human body weight is mineral matter, vital to all mental & physical processes & for our well being.

(xvi) Ans: (c) Hemoglobin

Hemoglobin is present in blood. It carries oxygen from lungs to all parts of the body.

(xviii) Ans: (a) Fatty Acids

Soaps are sodium or potassium salts of long chain fatty acids.

**Q2: Give brief answers for the following questions.**

(i) What do you understand by the word 'Biochemistry'?

Biochemistry is the branch of science concerned with studying the various molecules that occur in living cells and organisms, with their chemical reactions.

Biology is the science of living organisms and chemistry is the science of atoms and molecules. So, biochemistry is the science of the atoms and molecules in living organisms.

(ii) Briefly state the functions of Carbohydrates.

The main functions of carbohydrates are given below:

- These are source of energy.
- These are necessary for proper fat metabolism.
- These are the only source of energy for the brain and nerve tissues.
- Some carbohydrates support the growth of healthy bacteria in the intestines for digestion.
- Some carbohydrates high in fibre helps prevent constipation and lowers the risk for cancer, heart disease and diabetes.
- They are storehouse of energy. e.g. starch is the food stores in plants and glycogen in animals.
- They build the structure of plants and animals as cellulose or pectin.



Unit 21: Biochemistry

**Name the classes and sub-classes of Proteins.**

Proteins are classified into three types

- (A) **Simple Proteins:** e.g. Albumins; Globulins; Glutelins; Histones; Scleroproteins;
- (B) **Conjugated proteins:** e.g. Nucleoproteins; Mucoprotein; Glycoprotein; Phosphoprotein;
- (C) **Derived proteins:** e.g. Proteans; Proteases; Peptones; Peptides;

**In a range of 0-35°C, the rate of reaction of an enzyme is proportional to temperature. Justify it.**

- When temperature rises to 35°C, heat adds in the activation energy and also provides kinetic energy for the reaction. So reactions are accelerated.
- However, when temperature is raised well above this, heat energy increases the vibrations of atoms of enzyme. Thus, the globular structure of enzyme is lost. It results in a rapid decrease in rate of enzyme action.

**How does pH affect enzyme Activity?**

- All enzymes work at their maximum rate at a narrow range of pH, called as the optimum pH.
- Change in pH can affect the ionization of the amino acids at the active site. Thus, enzymes activity is lost.
- Every enzyme has its specific optimum pH value.  
e.g. pepsin (working in stomach) is active in acidic medium (low pH)

**Describe lock and key mechanism of enzyme action.**

In 1894, a German chemist, Emil Fischer proposed lock and key model.

According to this model, both enzyme and substrate possess specific shapes that fit exactly into one another. This model explains enzyme specificity. Thus a specific enzyme catalyzes acts on a specific substrate only.

e.g. lipase enzyme acts on lipids and digests them into fatty acids and glycerol. It cannot act on proteins

**(vi) What is the main use of enzymes in paper industry?**

Enzymes break starch to lower its viscosity that aids in making paper.

**(vii) Define cofactor and co-enzymes.**

The non-protein part of enzyme is called co-factor or co-enzyme.

Without cofactor enzyme cannot work. So, they are required by all enzymes.

Co-factors include inorganic ions, complex organic or organo-metallic molecules.

- $Fe^{2+}$  ions are cofactor for chrome oxidase enzyme, etc.
- Nicotinamide adenine dinucleotide (NAD) contains nicotinamide vitamin cofactor, etc.

**(viii) Shortly explain the only property that all the Lipids have in common.**

Naturally occurring organic compounds of animals and plants origin, which are soluble in organic solvents are called lipids.

All lipids are hydrophobic. This is the one property they have in common. This group of molecules includes fats and oils, waxes, phospholipids, steroids (like cholesterol), and some other related compounds.

**(ix) Explain the structural components of DNA and RNA.**

Both DNA and RNA are polymers of nucleotides.

The nucleotide consists of: one sugar, one nitrogenous base, and at least one phosphate.

**Sugar:** In DNA, it is deoxyribose sugar and in RNA it is ribose sugar.

**Nitrogen bases:** In DNA, four nitrogenous bases are: Adenine, Guanine, Cytosine and Thiamine

In RNA, four nitrogenous bases are: Adenine, Guanine, Cytosine and Uracil

**Phosphate:** The phosphate is similar in both DNA and RNA.



(xi) Define Lipids and state the difference between fat and oil.

Naturally occurring organic compounds of animals and plants origin, which are soluble in organic solvents are called lipids. They are water insoluble.

Fats	Oils
(1) They are obtained from animals	(1) They are obtained from plants
(2) They are saturated	(2) They are unsaturated
(3) They are solid or semi-solid at room temperature	(3) They are liquid at room temperature
(4) They possess high melting points	(4) They possess low melting points
(5) They have low iodine number (a test for unsaturation).	(5) They have high iodine number. It is because higher the iodine number, higher the unsaturation.

(xii) Briefly state how Vitamin D is formed in human body?

When ultraviolet light falls upon 7-dehydrocholesterol it is converted into vitamin D. This molecule is present naturally in the skin of animals. So, if the skin is exposed to UV rays (present in sun rays to some extent), this material is converted into vitamin D.

(xiii) State the differences between the chemical structures of DNA and RNA.

They differ in following ways.

- The sugar in RNA is ribose while the sugar in DNA is 2-deoxyribose.
- Four different bases are found in DNA cytosine (C) thiamine (T) adenine (A) and guanine (G). In RNA thiamine does not occur and its place is taken by uracil (U).
- DNA is nearly always double stranded, while RNA is usually single strand.
- DNA is used to store information while RNA is used to transfer information

(xiv) Briefly state why minerals are important for human life.

- They are constituents of the teeth, bones, tissues, blood, muscle, and nerve cells.
- Many of them act as catalysts for many biological reactions within the human body.
- They are necessary for transmission of messages through the nervous system, digestion, & metabolism.
- Vitamins cannot be properly assimilated without the correct balance of minerals. e.g. calcium is needed for vitamin "C" utilization etc.

(xv) Name different routes for the loss of Zinc from human body.

- Loss of zinc through gastrointestinal tract accounts for approximately half of all zinc eliminated from the body.
- Considerable amount of zinc is secreted through the biliary and intestinal secretions but most of it is reabsorbed.
- Other routes of zinc excretion include the urine and surface losses (desquamated skin, hair, sweat).

**Q3: Give detailed answers for the following questions.**

(i) Describe different classes of Carbohydrates.

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(ii) Explain the structure of Proteins.

Page 396

(iii) Briefly describe the factors that affect the Activity of enzymes.

Page 400

(iv) What is the nutritional importance of Lipids?

Page 406

(v) Explain the structures of Nucleic acids.

Page 409

(vi) Describe four important minerals and their sources.

Page 412



**YOUR SKILLS**

**Marks: 85**

**20 Minutes**

**OBJECTIVE**

**Marks: 17**

Over writing, cutting, erasing, using lead pencil will result in loss of marks

Circle the correct option i.e. A/B/C/D. Each part carries one mark.

Carbohydrates are ..... Compounds of aldehydes & Ketoses

(a) carbonyl (b) polyhydroxy (c) hydroxy (d) All of these

Which of the following is not a carbohydrate

(a) ribose (b) glucose (c) mannose (d) formaldehyde

What is general formula of carbohydrates

(a)  $C_n(H_2O)_{n+1}$  (b)  $C_n(HO)_n$  (c)  $C_n(H_2O)_n$  (d)  $C(H_2O)_n$

Which one of the following carbohydrates does not hydrolyse?

(a) ribose (b) glucose (c) galactose (d) None

Which carbohydrate is present in grapes

(a) glucose (b) fructose (c) both (d) None

Which of the following is present in milk?

(a) galactose (b) lactose (c) glucose (d) both a & b

One glucose molecule combine with galactose molecule through glycosidic linkage to form

(a) sucrose (b) starch (c) galactose (d) lactose

Which one of the following is a polysaccharide?

(a) cellulose (b) starch (c) both a & b (d) galactose

1 gram of fat contains approximately

(a) 4 k cal (b) 9 cal (c) 9 k cal (d) 9 J

Macromolecules are of has many types?

(a) 3 (b) 4 (c) 5 (d) 6

Prosthetic groups are

(a) Required by all enzymes (b) loosely attached with enzymes (c) protein in nature (d) Tightly bound to enzyme

Lipids are generally defined in terms of

(a) solubility (b) structure (c) Molarity (d) all of these

Minerals constitute ..... of human body weight

(a) 10 % (b) 100 % (c) 5 % (d) 50 %

..... is part of enzyme glutathione peroxidase.

(a) Zn (b) Se (c) Mo (d) K

In adults ..... of iodide absorbed is trapped by thyroid gland.

(a) 50 % (b) 70 % (c) 80 % (d) 100 %

Which one of the following is considered as macro-mineral for body

(a) Iron (b) iodine (c) calcium (d) both a & c

Calcium has ..... stable isotopes.

(a) 7 (b) 9 (c) 6 (d) 11

**SUBJECTIVE**

**Total Marks Section B and C: 68**

**Section - B (Marks 42) (14 × 3 = 42)**

**Q2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines.**

- (i) (a) Define carbohydrates. (1)
- (b) All organic compounds which have general formula  $C_n(H_2O)_n$  are not carbohydrates. Justify. (2)
- (ii) Describe role of carbohydrates in living organisms. (3)
- (iii) (a) Define monosaccharides. (1)
- (b) What are source of monosaccharides. (2)
- (iv) (a) How monosaccharides are classified? (2)
- (b) What are polysaccharides. (1)
- (v) (a) Define disaccharides. (2)
- (b) What are sources of disaccharides. (2)
- (vi) (a) Define glycosidic linkage with example. (1)
- (b) What is glycemic index. (2)
- (vii) (a) Compare glycogen in starch. (1)
- (b) Draw structure of Amylose. (1.5)
- (viii) (a) What is chitin. (1.5)
- (b) What is source of children. (1)
- (ix) (a) What are bacterial polysaccharides?



- |  |       |
|--|-------|
| (b) What is role of bacterial polysaccharide in living organisms?    | (2)   |
| (a) What are globulins.  | (2)   |
| (b) What is source of Gluten?  | (1)   |
| (i) What are conjugated Proteins.                                    | (3)   |
| (ii) How quaternary structure of protein is formed?                  | (3)   |
| (a) What is haemoglobin.   | (1)   |
| (b) Differentiate between Anabolism & Catabolism.                    | (2)   |
| (a) Describe Lock and Key model.                                     | (2)   |
| (b) What are enzymes.  | (1)   |
| (a) How does Induce - Fit Model describe mechanism of enzyme Action. | (1.5) |
| (b) Enzymes are specific in their action. Justify.                   | (1.5) |
| (a) What is optimum temperature for enzyme?                          | (1)   |
| (b) How does temperature affect enzymatic activity.                  | (2)   |
| (a) What are inhibitors?   | (1)   |
| (b) Describe types of inhibitors.                                    | (2)   |
| (a) What is spring myelin?   | (1)   |
| (b) What are fatty acids?  | (2)   |
| (a) What is saponification.  | (1.5) |
| (b) What is meant by hardening of oil.                               | (1.5) |

**Section - C**

**Note:** Attempt any TWO questions. All questions carry equal marks. ( $2 \times 13 = 26$ )

- |   |     |
|---|-----|
| Q3. (a) Discuss functions of Polysaccharides.             | (5) |
| (b) Describe the structure of Proteins.                   | (4) |
| (c) How enzymes work as biocatalyst.                      | (4) |
| Q4. (a) Classify Proteins.                                | (5) |
| (b) What are the factors which affect enzymatic activity. | (4) |
| (c) How inhibitors decrease the enzymatic activity.       | (4) |
| Q5. (a) Explain the structure of Lipids.                  | (5) |
| (b) Differentiate between DNA & RNA.                      | (4) |
| (c) What is role of minerals in our body?                 | (4) |



## CHAPTER # 22

# INDUSTRIAL CHEMISTRY



### INTRODUCTION:

#### Definition:

The branch of chemistry which applies physical and chemical procedures towards the transformation of natural raw materials and their derivatives to products that are of benefit to humanity is called Industrial Chemistry.

#### Development of Industrial Chemistry

- The scientists thought how various chemicals are produced in much more quantity than the laboratory scale. This thinking started the development of industrial chemistry.
- Chemistry knowledge was applied to furnish the rapidly expanding chemical industries with "recipes". These recipes are now called chemical processes.
- Industrial chemistry keeps up with the progress in science and technology. It incorporates other emerging disciplines such as biotechnology, microelectronics, pharmacology and material science.
- It is also concerned with economics and the need to protect the environment.

#### The link between Classical and Industrial Chemistry

- The Classical Chemistry (organic, inorganic and physical chemistry) is very essential for advancing the science of chemistry. It discovers and and report new products, routes and techniques.
- The Industrial Chemistry helps us to close the gap between classical chemistry as it is taught in colleges and universities, and chemistry as it is practiced commercially.

#### Scope of Industrial Chemistry

- The scope of industrial chemistry therefore includes:
  - ✓ The use of materials and energy in appropriate scale
  - ✓ Application of science and technology to enable humanity experiences the benefits of chemistry in different areas: food production, health and hygiene, shelter, protection, decoration, recreation and entertainment.

### INTRODUCTION TO THE CHEMICAL INDUSTRY

The chemical industry can also be classified according to the type of main raw materials used and/or type of principal products made.

#### (1) Industrial inorganic chemical industries

Industrial inorganic chemical Industries extract inorganic chemical substances, make composites of the same and also synthesize inorganic chemicals.

#### (2) Industrial organic chemical industries.

- Heavy industrial organic chemical industries produce petroleum fuels, polymers, petrochemicals and other synthetic materials, mostly from petroleum.
- Light organic industries produce specialty chemicals which include pharmaceuticals, dyes, pigments and paints, pesticides, soaps and detergents, cosmetic products and miscellaneous products.



## THE STRUCTURE OF THE GLOBAL CHEMICAL INDUSTRY

- Normally a value is given to something according to its importance.
- Some things are of high value while others are of low value.
- The low valued products are needed to produce in large volumes to make significant profit. This means that the raw materials are cheap and easily accessible. There is also an existing, relatively simple, and easily accessible processing technology.
- To sell a large volume of product, there must be a large market. This brings stiff competition which also makes the price to remain low.

### COMMODITY CHEMICALS:

*Commodity chemicals are defined as low-valued products produced in large quantities mostly in continuous processes. They are of technical or general purpose grade.*

- The global chemical industry is founded on basic inorganic chemicals (BIC) and basic organic chemicals (BOC) and their intermediates. It is because they are produced directly from natural resources or immediate derivatives of natural resources. They are produced in large quantities.
- Some of the top ten BIC are: sulphuric acid, nitrogen, oxygen, ammonia, lime, sodium hydroxide, phosphoric acid and chlorine. The sulphuric acid is always number one. It is because it is used in the manufacture of fertilizers, polymers, drugs, paints, detergents and paper. It is also used in petroleum refining, metallurgy and in many other processes. The top ranking of oxygen is due to its use in the steel industry.
- Among top ten BOC are Ethylene and propylene. They are used in the production of many organic chemicals including polymers.
- BIC and BOC are referred to as commodity or industrial chemicals.

### SPECIALTY CHEMICALS:

*High-value adding involves the production of small quantities of chemical products for specific end uses. Such products are called specialty chemicals.*

- These are high value-added products produced in low volumes and sold on the basis of a specific function.

#### Example:

**Performance chemicals:** These are high value products produced in low volumes and used in extremely low quantities. They are judged by performance and efficiency. Enzymes and dyes are performance chemicals.

#### Other Examples:

medicinal chemicals, agrochemicals, pigments, flavour and fragrances, personal care products, surfactants and adhesives.

- Specialty chemicals are mainly used in the form of formulations.
- Purity is of vital importance in their formulation. Thus highly valued pure chemicals must be prepared known as fine chemicals

### FINE CHEMICALS:

*They are high value-added pure organic chemical substances produced in relatively low volumes and sold on the basis of exact specifications of purity rather than functional characteristics.*

The raw materials for a product need to be very pure for the product to function as desired.

#### Examples:

Research chemicals, pharmaceutical ingredients, etc.

**The global market share for each type is roughly as follows:**

**Commodities = 80%**

**Specialties Chemicals = 18%**

**Fine Chemicals = 2%**



**Exercise Q3 (i): What is chemical industry? Discuss different raw materials used in this industry.**  
The chemical industry comprises the companies that produce industrial chemicals

### RAW MATERIAL FOR THE CHEMICAL INDUSTRY

- All chemicals are derived from raw materials available in nature.
- The price of chemicals depends on the availability of their raw materials.
- Major chemical industries have therefore developed around the most plentiful raw materials
- The natural environment is the source of raw materials for the chemical industry.

### RAW MATERIALS FROM THE ATMOSPHERE

- The atmosphere is the field above ground level.
- It is the source of air from which six industrial gases ( $N_2$ ,  $O_2$ , Ne, Ar, Kr and Xe) are manufactured.
- The mass of the earth's atmosphere is approximately  $5 \times 10^{15}$  tons. Therefore the supply of the gases is almost unlimited.

### RAW MATERIALS FROM THE HYDROSPHERE

- Ocean water is about  $1.5 \times 10^{21}$  litres.
- It contains about 3.5 percent by mass dissolved material.
- Seawater is a good source of sodium chloride, magnesium and bromine.

### RAW MATERIALS FROM THE LITHOSPHERE

- The vast majority of elements are obtained from the earth's crust in the form of mineral ores, carbon and hydrocarbons.
- Coal, natural gas and crude petroleum are used as energy sources. These are also converted to thousands of chemicals.

### RAW MATERIALS FROM THE BIOSPHERE

- Vegetation and animals contribute raw materials to the so-called agro-based industries.
- Oils, fats, waxes, resins, sugar, natural fibres and leather are examples of thousands of natural products.

## QUICK QUIZ-1:

(1) Name those disciplines which play important role in industrial chemistry

The industrial chemistry has a strong link with the Classical Chemistry which includes organic, inorganic and physical chemistry. The classical chemistry discovers and report new products, routes and techniques which are then used in industrial chemistry. The industrial chemistry also includes disciplines such as biotechnology, microelectronics, pharmacology and material science.

(2) Define Industrial chemistry

The branch of chemistry which applies physical and chemical procedures towards the transformation of natural raw materials and their derivatives to products that are of benefit to humanity is called Industrial Chemistry.

(3) What is difference between organic and inorganic chemical industries?

- The organic chemical industry is based upon compounds of carbon. These may be of plants and animals origin or may be synthetic. e.g. polymers, petrochemicals, dyes, paints, pesticides, soaps etc.
- The inorganic chemical industries are largely based upon compounds of elements other than carbon. It extract inorganic chemical substances, make composites of the same and also synthesize inorganic chemicals.



4) What type of products are obtained from heavy and light organic industries?

- Heavy industrial organic chemical industries produce petroleum fuels, polymers, petrochemicals and other synthetic materials, mostly from petroleum.
- Light organic industries produce specialty chemicals which include pharmaceuticals, dyes, pigments and paints, pesticides, soaps and detergents, cosmetic products and miscellaneous products.

5) What raw material are obtained from atmosphere

The atmosphere is the source of air from which six industrial gases ( $N_2$ ,  $O_2$ ,  $Ne$ ,  $Ar$ ,  $Kr$  and  $Xe$ ) are manufactured.

6) In which ratio dissolved materials are present

Ocean water is about  $1.5 \times 10^{21}$  litres. It contains about 3.5 percent by mass dissolved material.

7) Give few natural products

Oils, fats, waxes, resins, sugar, natural fibres etc.

8) Give examples of Basic organic chemicals

Some of the top ten BOC are: sulphuric acid, nitrogen, oxygen, ammonia, lime, sodium hydroxide, phosphoric acid and chlorine.

9) What do you mean by commodity chemicals

Commodity chemicals are defined as low-valued products produced in large quantities mostly in continuous processes. They are of technical or general purpose grade.

These include

Basic inorganic chemicals (BIC) such as sulphuric acid, oxygen, ammonia etc.

Basic organic chemicals (BOC) such as ethylene, propylene etc.

10) What is meant by performance chemicals

These are high value products produced in low volumes and used in extremely low quantities. They are judged by performance and efficiency. Enzymes and dyes are performance chemicals.

11) Give share of different types of chemicals in global market.

The global market share for each type is roughly as follows:

Commodities = 80%

Specialties Chemicals = 18%

Fine Chemicals = 2%

## SAFETY CONSIDERATIONS IN PROCESS INDUSTRIES

### INTRODUCTION

Process safety technology has played an important role in the chemical processing industries. Thus, handling flammable and combustible liquids and gases could proceed without undesirable consequences.

e.g. During the 1980s, the oil and gas industries recognized that only process safety technology is not sufficient to prevent tragic incidents. The process safety management is also needed. So, a number of industrial associations initiated programmes to develop and provide process safety management guidelines for use by their members. For example these associations are: in the United States, the Centre for Chemical Process Safety (CCPS), the American Petroleum Institute (API) and the Chemical Manufacturers' Association (CMA).

### PROCESS SAFETY MANAGEMENT REQUIREMENTS

- Process safety management is an integral part of the overall chemical processing facility safety programme.
- An effective process safety management programme requires the leadership, support and involvement of top management, facility management, supervisors, employees, contractors and contractor employees.



## **ELEMENTS OF THE PROCESS SAFETY MANAGEMENT PROGRAMME**

There are a number of basic requirements which should be included in every chemical process safety management programme:

### **(1) Process Safety Information**

- Process safety information is used by the process industry to define critical processes, materials and equipment.
- It includes all available written information about process technology, process equipment, raw materials and products. It also includes the information about chemical hazards before conducting a process hazard analysis.
- Other critical process safety information is documentation relating to capital project reviews and design basis criteria.

### **(2) Employee Involvement**

- Process safety management programmes include employee participation in the development and conduct of process safety analyses and other elements of the programme.
- Access to process safety information, incident investigation reports and process hazard analyses is usually provided to all employees and contractor employees working in the area.
- Most industrialized nations require that workers be systematically instructed in the identification, nature and safe-handling of all chemicals to which they may be exposed.

### **(3) Process Hazard Analysis**

- After the process safety information is compiled, a thorough process hazard analysis is carried out.
- It includes systematic multi-disciplinary process hazard analysis, appropriate to the complexity of the process.
- It is conducted in order to identify, evaluate and control the hazards of the process.
- Persons performing the process hazard analysis should be knowledgeable and experienced in relevant chemistry, engineering and process operations.
- Each analysis team normally includes at least one person who is thoroughly familiar with the process being analysed and one person who is competent in the hazard analysis methodology being used.

### **(4) Management of Change**

- Chemical process facilities should develop and implement programmes which provide for the revision of process safety information, procedures and practices as changes occur.
- Such programmes include a system of management authorization and written documentation for changes to materials, chemicals, technology, equipment, procedures, personnel and facilities that affect each process.

### **(5) Operating Procedures**

- Chemical processing facilities must develop and provide operating instructions and detailed procedures to workers.
- Operating instructions should be regularly reviewed for completeness and accuracy (and updated or amended as changes occur) and cover the process unit's operating limits.

### **(6) Safe Work Practices**

- Chemical process facilities should implement hot-work and safe work permit and work order programmes to control work conducted in or near process areas.
- Supervisors, employees and contractor personnel must be familiar with the requirements of the various permit programmes. These include permit issuance and expiration and appropriate safety, materials handling and fire protection and prevention measures.

### **(7) Employee Information and training**

- Chemical process facilities should use formal process safety training programmes to train and educate, reassigned and new supervisors and workers.
- The training provided for chemical process operating and maintenance supervisors and workers should be comprehensive.



## QUICK QUIZ-2:

(1) **What are requirement of process safety management**

An effective process safety management programme requires the leadership, support and involvement of top management, facility management, supervisors, employees, contractors and contractor employees.

(2) **How employees should be involved in safety management programme**

- Under safety management, access to process safety information, incident investigation reports and process hazard analyses is usually provided to all employees and contractor employees working in the area.
- Some countries also provide instruction in the identification, nature and safe-handling of all chemicals to which they may be exposed

(3) **What is analysis team**

Each analysis team normally includes at least one person who is thoroughly familiar with the process being analysed and one person who is competent in the hazard analysis methodology being used.

(4) **What is role of management of change in process industries?**

- Chemical process facilities should develop and implement programmes which provide for the revision of process safety information, procedures and practices as changes occur.
- Such programmes include a system of management authorization and written documentation for changes to materials, chemicals, technology, equipment, procedures, personnel and facilities that affect each process.

**Exercise Q3 (ii): What are dyes? How are they classified on the basis of structure?**

## DYES

A dye is a coloured compound, normally used in solution, which is capable of being fixed to a fabric.

The dye must be 'fast' or chemically stable so that the color will not wash with soap and water, or fade on exposure to sunlight (ultraviolet light).

- The dye color is due to the presence of a chromophore.
- Its fixing property is due to the acidic or basic auxochromic groups such as OH, SO<sub>3</sub>H, NH<sub>2</sub>, NR<sub>2</sub>, etc
- The polar auxochrome makes the dye water-soluble and binds the dye to the fabric by interaction with the oppositely charged groups of the fabric structure.

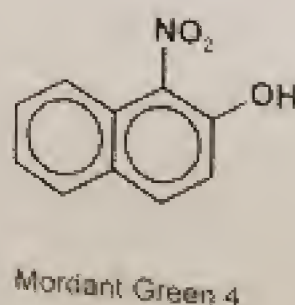
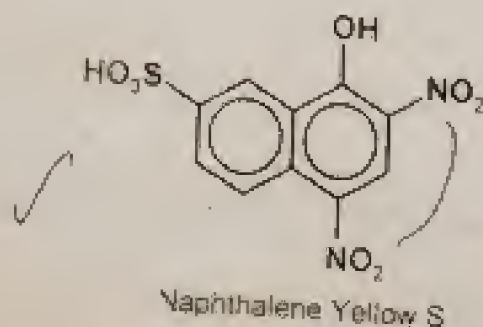
## CLASSIFICATION OF DYES BY STRUCTURE

Dyes are classified according to the type of chromophores present in their structures. This method of classification includes the following main types:

### (I) NITRO AND NITROSO DYES:

The NO<sub>2</sub> and NO groups are chromophores in this class of dyes.

**Examples:**





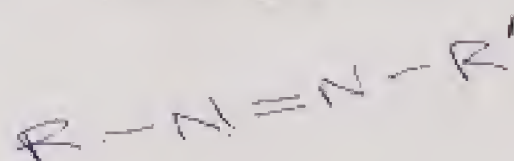
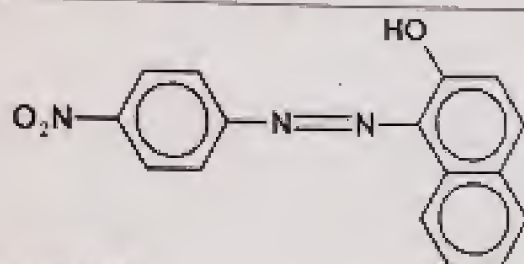
Unit 22: Industrial Chemistry

**AZO DYES:**

- The azo dyes contain one or more azo groups,  $-N=N-$  as the primary chromophore.
- The common auxochromes are  $NH_2$ ,  $NR_2$ ,  $OH$ ,  $SO_3H$ , etc.
- Azo dyes form the largest and most important group of synthetic group of synthetic dyes. They are highly colored.
- They can be prepared by diazotising an aromatic amine to produced diazonium salt. It is then coupled to a compound series. Thus, azo dyes can be produced with almost any color.

**Examples**

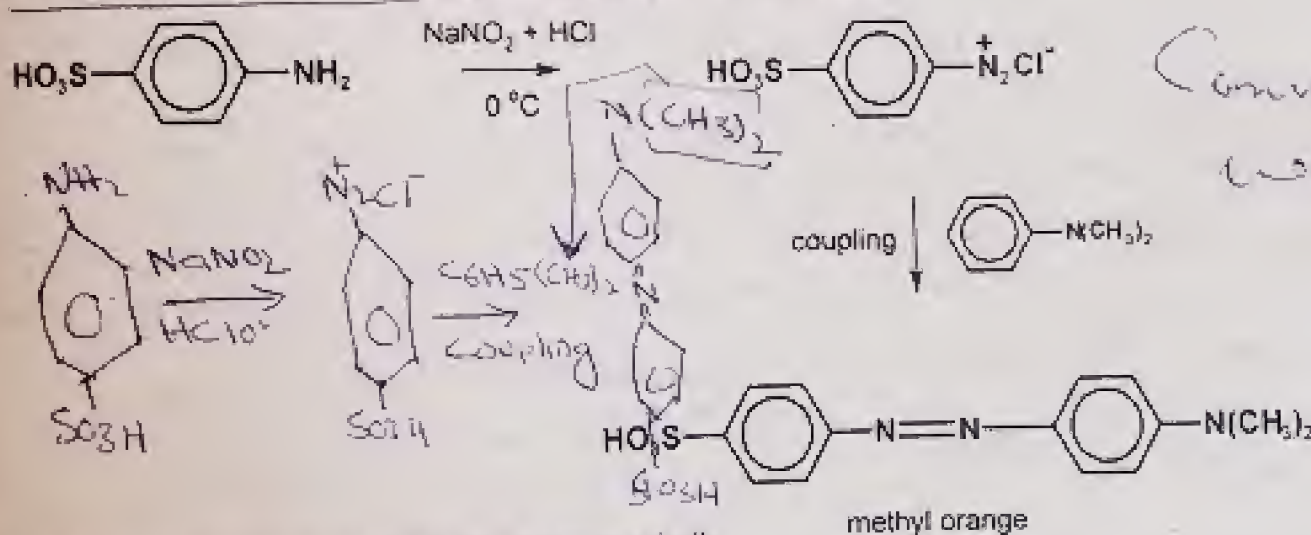
**(i) Para Red**



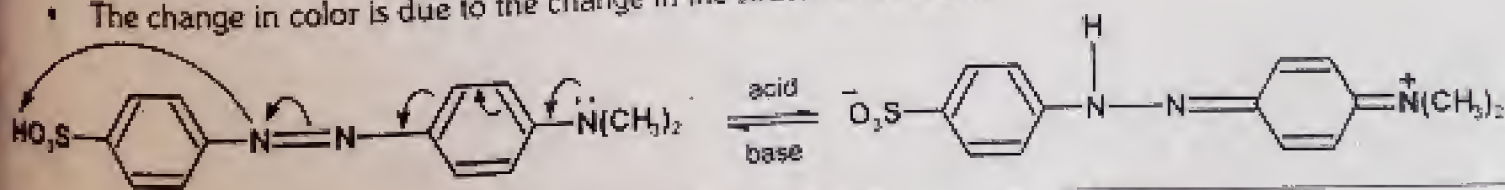
- It was the first azo dye to be prepared.
- Para red is obtained by the reaction of diazotized p-nitroaniline with  $\beta$ -naphthol on fabric itself.

**(ii) Methyl Orange:**

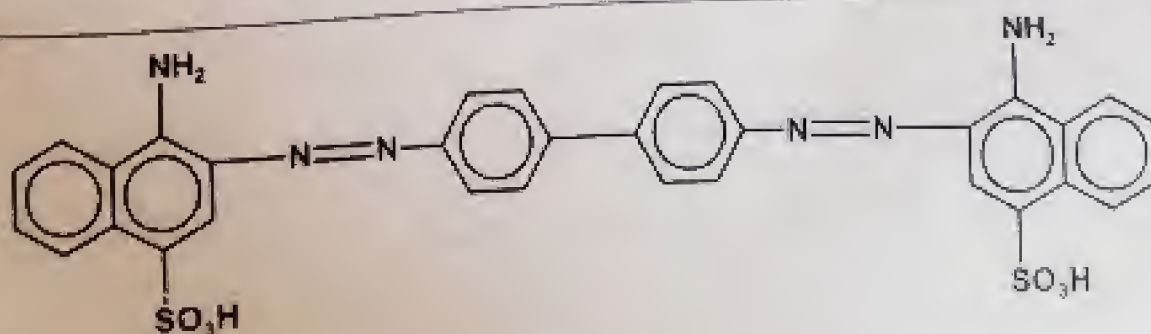
- Methyl orange is obtained from sulphanilic acid by the following steps:



- Methyl orange imparts orange color to wool and silk.
- However, the color is not fast to sunlight or washing.
- It is a valuable indicator for acid-base titrations because it gives yellow color in basic solution and red color in acid solution.
- The change in color is due to the change in the structure of the ions.



**(iii) Congo Red**



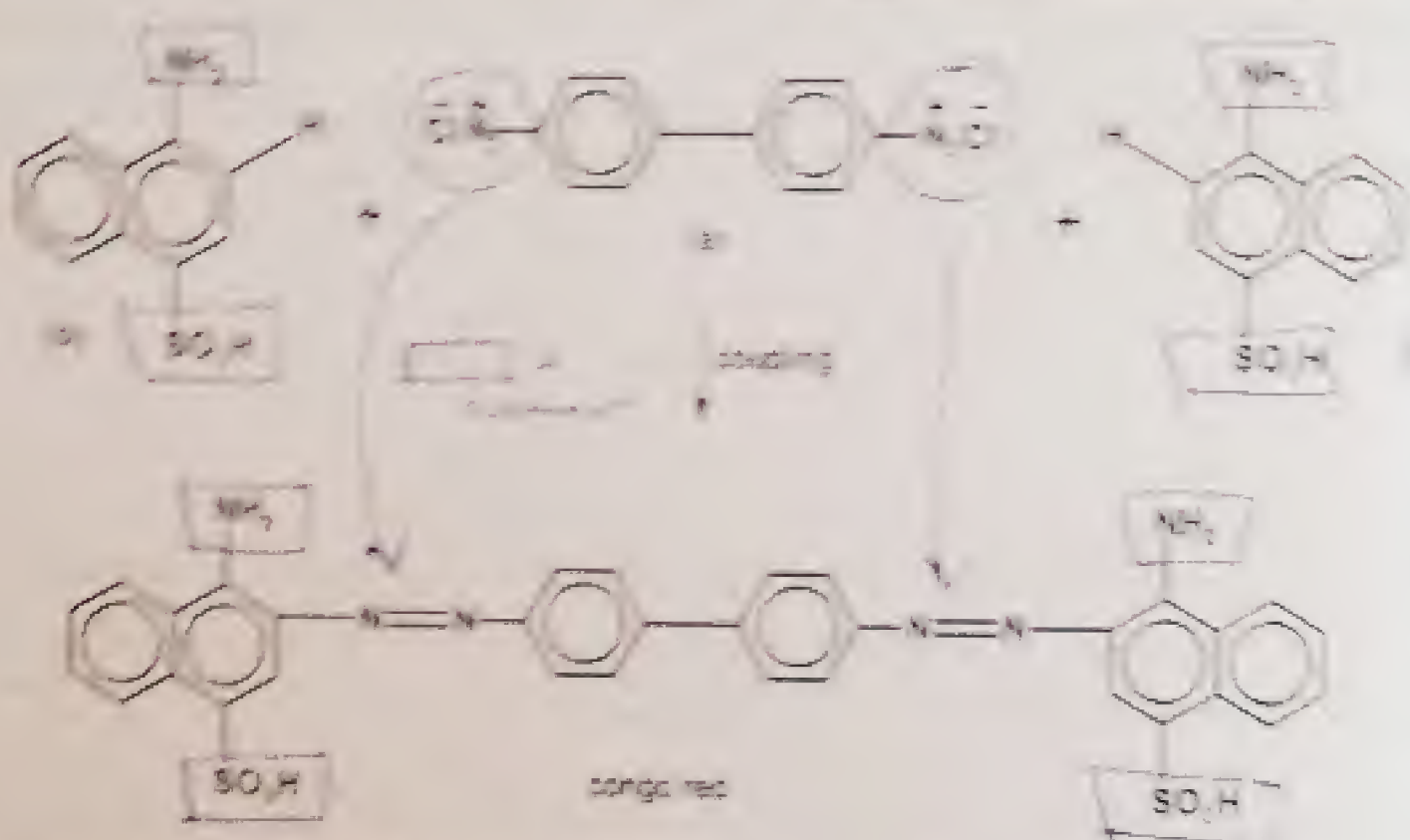


Unit 8: Organic Chemistry

10

College Chemistry: Organic Chemistry

- It is a direct dye and its sodium salt is used for dyeing cotton red from aqueous solutions.
- Congo red is also used as an indicator, being red in alkali and blue in acid solutions.



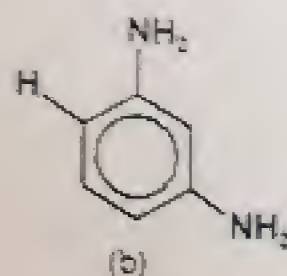
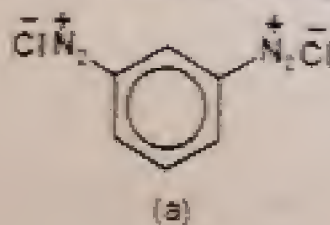
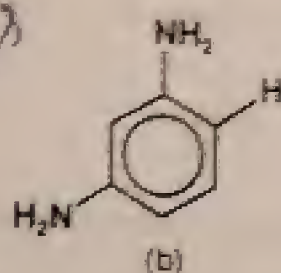
- It is a direct dye and its sodium salt is used for dyeing cotton red from aqueous solutions.
- Congo red is also used as an indicator, being red in alkali and blue in acid solutions.

#### (d) Bismarck Brown

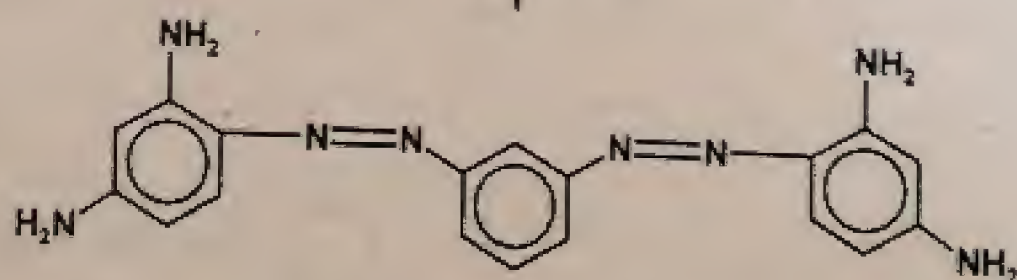
- It is obtained by coupling tetrazotized m-diaminobenzene (a) with two molecules of m-diaminobenzene (b).
- Bismarck brown is a brown dye used in boot polishes and for dyeing wool and cotton.

3 hands

2 Hands



coupling



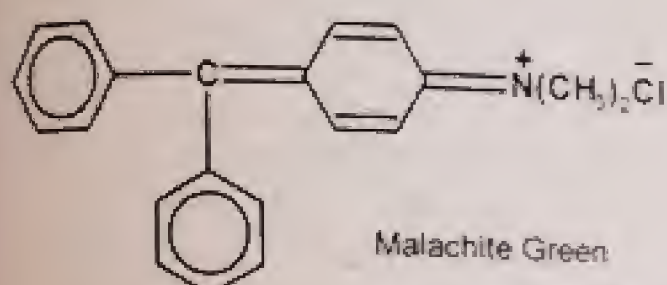
Bismarck Brown



### TRIARYLMETHANE DYES:

- In triarylmethane dyes, a central carbon is bonded to three aromatic rings one of which is in the quinoid form (the chromophore).
- The auxochromes are  $-NH_2$ ,  $-NR_2$  and  $-OH$ . Examples are.

#### Malachite Green:

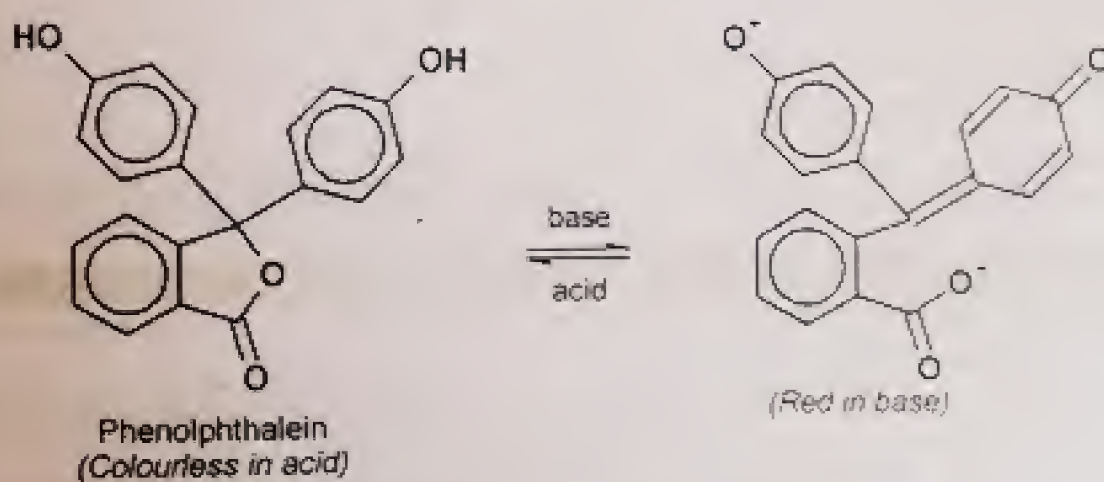


Green-Blue  
5-1

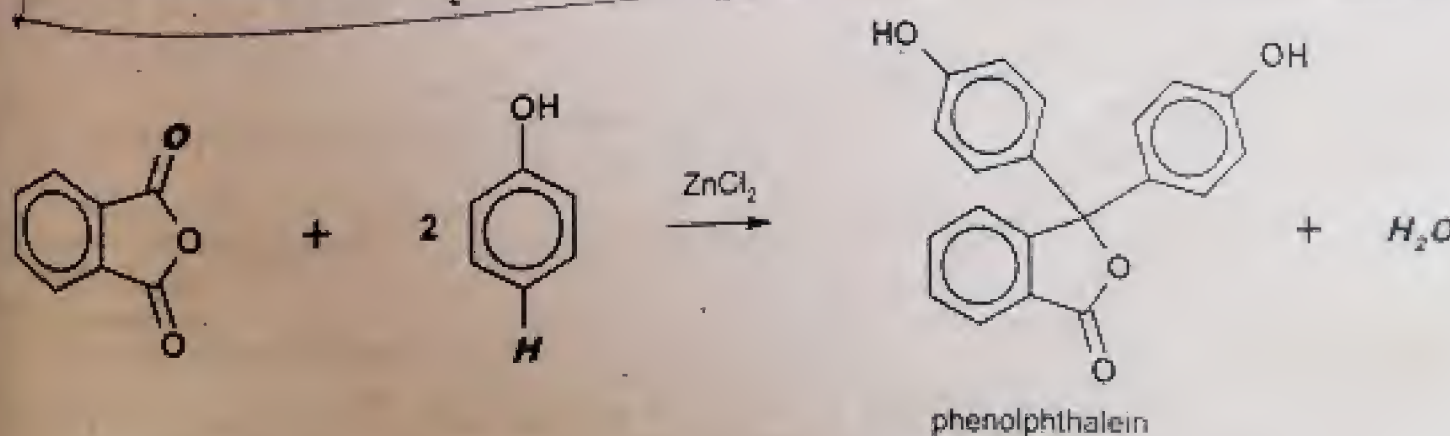
- Malachite green has a deep green-blue color.
- Although the color fades in light, malachite green is used as a direct dye for wool and silk.

#### Phenolphthalein:

- It is also a triarylmethane dye but it is better known as an acid-base indicator.
- It shows red colour in base and colourless in acid.



- Phenolphthalein is prepared by heating phthalic anhydride (1 mole) and phenol (two moles) in the presence of anhydrous zinc chloride at  $120^\circ\text{C}$ .

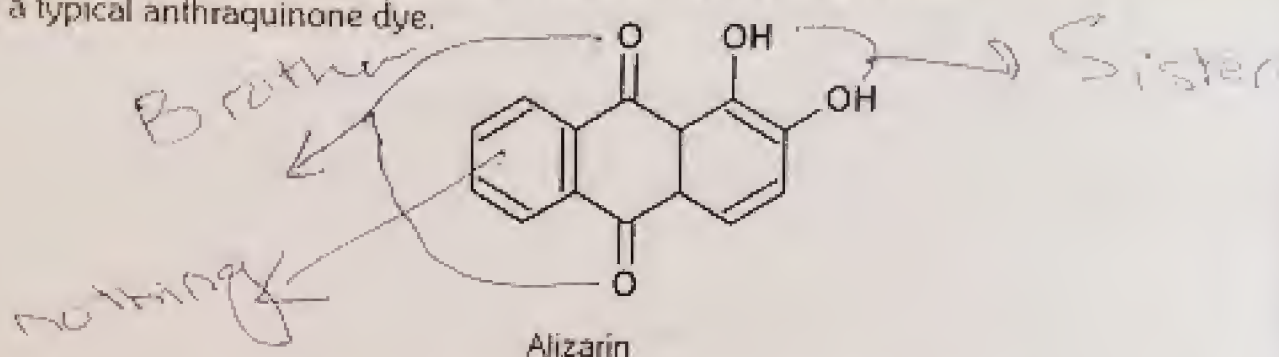


Color



#### (4) ANTHRAQUINONE DYES:

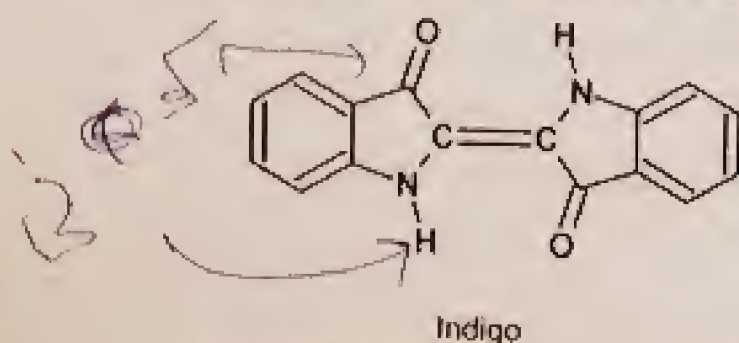
- The para quinoid chromophore is present in these anthracene-type dyes.
- Alizarin is a typical anthraquinone dye.



- Alizarin forms ruby red crystals which dissolve in alkali to give purple solutions.
- It is used to dye wool and cotton.

#### (5) INDIGO DYES:

- Indigo is an example of the type of dyes which contain carbonyl chromophore.



- It is a dark-blue crystalline compound, insoluble in water.
- It is used for dyeing cotton by the Vat Process.

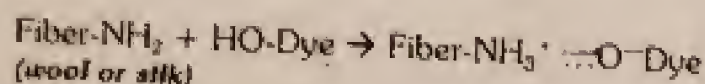
**Exercise Q3 (III):** What do you know about dyes? How are they classified on the basis of application?

#### CLASSIFICATION OF DYES BY METHODS OF APPLICATION

- The chemical classification of dyes is of interest to the chemist but the dyer is concerned mainly with application of dyes to fabrics.
- The method used for application in a particular case depends on the nature of both the dye and the fabric to be dyed.
- The dyes are often classified on the basis of technique employed for their application.

##### (1) DIRECT DYES:

- These can be applied to a fabric by direct immersion in a water solution of the dye.
- A direct dye contains acidic or basic auxochrome which combines with the opposite polar group present in the chemical structure of the fiber.
- Wool and silk are readily dyed by this method.
- Martius Yellow, a typical direct dye, has the acidic auxochrome  $-OH$  which interacts with the basic group of wool or silk.



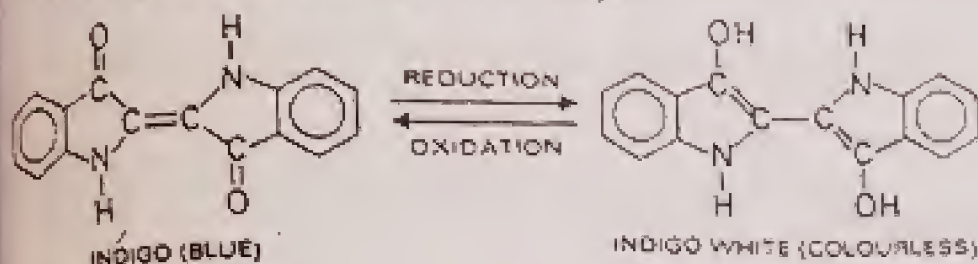
**Exercise Q3 (iv):** Write a note on  
(a) Vat Dyes  
(b) Mordant Dyes

##### (2) VAT DYES:

- These dyes are insoluble in water. However, on reduction with sodium hydrosulphide in a vat form a colorless soluble compound. This compound has a great affinity for cotton and other cellulose fibers.



- The cloth is soaked in the solution of a reduced dye and then hung in air, or treated with oxidants.
- As a result, the colorless compound is oxidized back to the insoluble dye which is now bound to the fabric.
- Indigo is a good example of a vat dye.

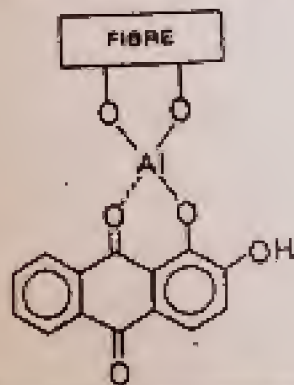


- Indigo blue has auxochromes -OH which bind the dye fast to the cellulose fiber that contains ethereal oxygen and OH groups by hydrogen bonding.

Exercise Q3 (iv): Write a note on:  
(c) Vat Dyes  
(d) Mordant Dyes

### (3) MORDANT DYES:

- This class of dyes has no natural affinity for the fabric and are applied to it with the help of salts e.g., oxides of aluminum or chromium. These salts are called Mordants.
- A fiber such as cotton is first treated with a mordant and then with the dye solution.
- The mordant forms an insoluble coordination complex between the fiber and the dye and binds the two.
- The insoluble complex compound appears in the form of lakes that are fast to light and washing.
- The mordant dyeing is the most suitable for wool and nylon.
- Alizarin is an example of a mordant dye.



*\* Auxochrome is a functional group of atoms with nonbonded electrons when attached to a chromophore.*

$\text{--- N=N ---} \xrightarrow{\text{NH}_2} \text{Auxochrome}$

*Chromophore*

### (4) AZOIC DYES (INGRAIN DYES):

- In this method of dyeing, the water insoluble azo dye is produced in the fabric itself.
- The cloth is first soaked in the solution of a coupling reagent usually a phenol or naphthol.
- It is then immersed in the solution of an auxochromes.
- The azoic dyeing is particularly suitable for cotton and other cellulosic fiber but may also be used for nylon.

### (5) DISPERSE DYES:

- These dyes are insoluble in water but can be dispersed in a colloidal form in water.
- The fabric is immersed in the colloidal dispersion of the dye.
- The fine dye particles are absorbed into the crystal structure of the fabric.
- Disperse dyes are used with modern synthetic fabrics such as nylon, orlon, polyester and cellulose acetate.

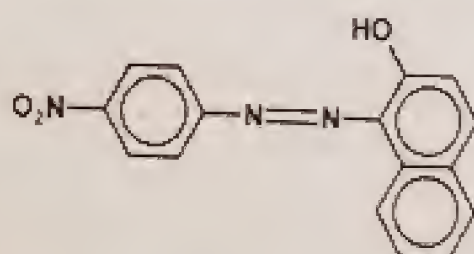
*\* Chromophore is a part of a molecule responsible for its colour.*



## QUICK QUIZ-3

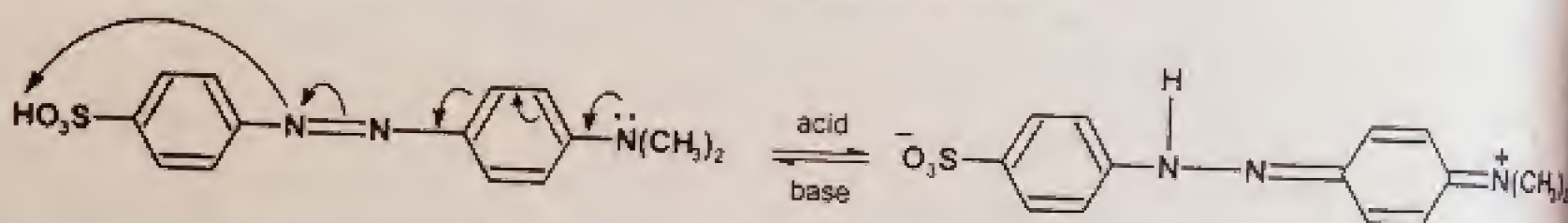
(1) Which one is first azo dye?

Para red is the first azo dye prepared by the reaction of diazotized p-nitroaniline with  $\beta$ -naphthol on fabric itself.



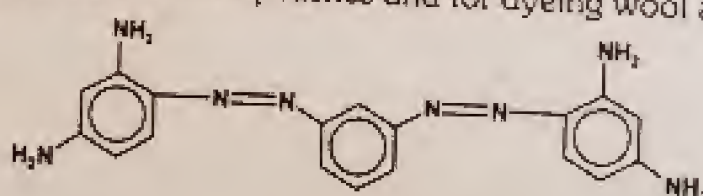
(2) What is the color of Methyl orange: (i) in acidic medium (ii) in basic medium

- Methyl orange is used as indicator for acid-base titrations. It is because it gives yellow color in basic solution and red color in acid solution.
- The change in color is due to the change in the structure of the ions.



(3) Which dye is used in boot polish and in dyeing wool and cotton?

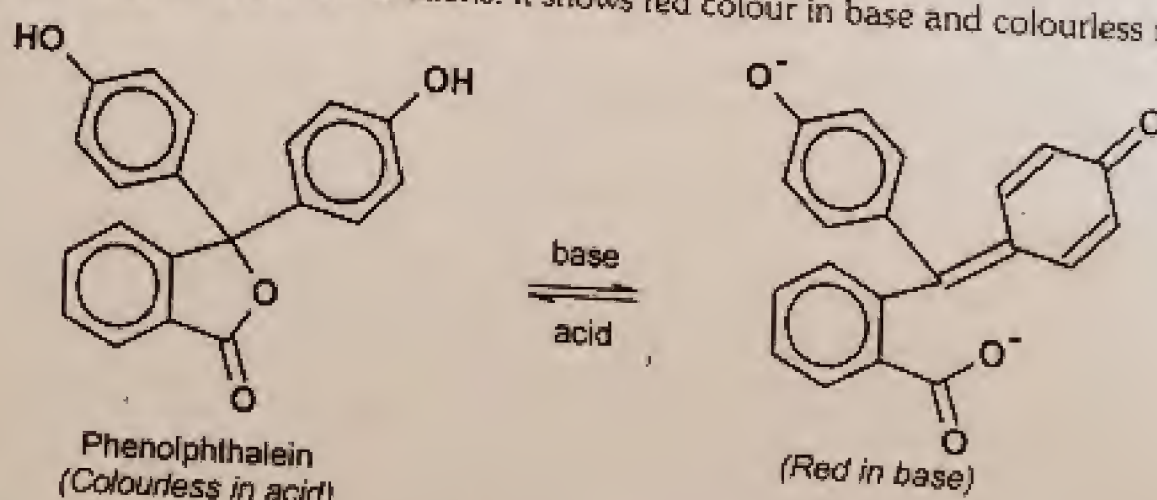
Bismarck brown is a brown dye used in boot polishes and for dyeing wool and cotton.



Bismarck Brown

(4) What is the color of phenolphthalein in (i) acidic medium (ii) basic medium

- It is used as indicator in acid-base titrations. It shows red colour in base and colourless in acid.



Phenolphthalein  
(Colourless in acid)

(Red in base)



Exercise Q3 (v): What is meant by Pesticides? Describe its types in detail.

## PESTICIDES

A pesticide is any chemical which is used by man to control pests. The pests may be insects, plant diseases, fungi, weeds, nematodes, snails, slugs, etc. Therefore, insecticides, fungicides, herbicides, etc., are all types of pesticides.

## TYPES OF PESTICIDES

### (1) INSECTICIDES

**Insecticides are chemicals used to control insects.**

- Often the word "insecticide" is confused with the word "pesticide." It is just one of many types of pesticides.
- An insecticide may kill the insect by touching it or it may have to be swallowed to be effective.
- Some insecticides kill both by touch and by swallowing.
- Insecticides called **Systemics** may be absorbed, injected, or fed into the plant or animal to be protected. When the insect feeds on this plant or animal, it ingests the systemic chemical and is killed.

### (2) MITICIDES AND ACARICIDES

**Miticides (or Acaricides) are chemicals used to control mites (tiny insecticide spider-like animals) and ticks.**

- The chemicals usually must contact the mites or ticks to be effective.
- These animals are so many and small, that great care must be used to completely cover the area on which the mites live.
- Miticides are very similar in action to insecticides and often the same pesticide kills both insects and mites.

### (3) FUNGICIDES

**Fungicides are chemicals used to control the fungi which cause molds, rots, and plant diseases.**

- All fungicides work by coming in contact with the fungus, because fungi do not "swallow" in the normal sense.
- Therefore, most fungicides are applied over a large surface area to try to directly hit every fungus.
- Some fungicides may be systemic in that the plant to be protected may be fed or injected with the chemical. The chemical then moves throughout the plant, killing the fungi.

### (4) HERBICIDES

**Herbicides are chemicals used to control unwanted plants.**

- These chemicals are a bit different from other pesticides. It is because they are used to kill or slow the growth of some plants, rather than to protect them.
- Some herbicides kill every plant they contact, while others kill only certain plants.
- It is of following types:

**Nonselective herbicides:**

- ✓ These are toxic to all plants.
- ✓ These are often used when no plants are wanted in an area, e.g. nonselective herbicides could be used for clearing under guardrails or for total control of weeds in industrial areas.

**Selective herbicides:**

- ✓ These kill some plants with little or no injury to other plants.
- ✓ Usually selective types will kill either broadleaved plants or grassy plants.
- ✓ These are useful for lawns, golf courses or in areas with desirable trees.
- ✓ Some very selective herbicides may kill only certain plants in a group, e.g., crabgrass killers on lawns.



## (5) RODENTICIDES

*Rodenticides are chemicals used to control rats, mice, bats and other rodents*

- Chemicals which control other mammals, birds, and fish are also grouped in this category by regulatory agencies
- Most rodenticides are stomach poisons and are often applied as baits
- They are usually not applied over large surfaces even if they act by contacting the pest. It is because of the hazard to domestic animals or desirable wildlife
- They are usually applied in limited areas such as runways, known feeding places, or as baits.

## (6) NEMATICIDES

*Nematicides are chemicals used to control nematodes.*

- Nematodes are tiny hair-like worms, many of which live in the soil and feed on plant roots
- Very few of these worms live above ground. U
- Usually, soil fumigants are used to control nematodes in the soil

## (7) MOLLUSCICIDES

*Molluscicides are chemicals used to control snails and slugs*

- Usually the chemicals must be eaten by the pest to work.
- Baits are often used to attract and kill snails or slugs in an area

## (8) REPELLENT

*A repellent is a pesticide that makes a site or food unattractive to a target pest*

- They are registered in the same way other pesticides are and must be used according to the label.
- Insect repellents are available as aerosols and lotions. These can be applied to skin, clothing, or plants to repel biting and nuisance insects.
- Vertebrate repellents are available as concentrates to be mixed with water, powders, and granules.
- They can be sprayed or painted on nursery crops, ornamental plantings, orchards, vineyards, vegetables and seeds. Repelling deer, dogs, birds, raccoons, and others can protect sites from damage.

## QUICK QUIZ-4

(1) Differentiate between

(i) Pesticides and Insecticides

- A pesticide is any chemical which is used by man to control pests. The pests may be insects, plant diseases, fungi, weeds, nematodes, snails, slugs, etc. Therefore, insecticides, fungicides, herbicides, etc., are all types of pesticides.
- Insecticide is a type of pesticide. It is used to kill control insects.

(ii) Fungicides and herbicides

- Fungicides are chemicals used to control the fungi which cause molds, rots, and plant diseases.
- Herbicides are chemicals used to control unwanted plants.

(2) What do you understand by systemics

**Systemics** are chemicals which are made to enter into the body **system** of living organisms by different ways. These may be absorbed, injected, or fed into the plant or animal to be protected. When the insect feeds on this plant or animal, it ingests the systemic chemical and is killed.

(3) How do herbicides differ from other pesticides?

These chemicals are a bit different from other pesticides. It is because they are used to kill or slow the growth of some plants, rather than to protect them.



**(4) Give different types of repellents.**

A repellent is a pesticide that makes a site or food unattractive to a target pest

e.g. Insect repellents are available as aerosols and lotions. These can be applied to skin, clothing, or plants to repel biting and nuisance insects.

**(5) What are molluscicides**

Molluscicides are chemicals used to control snails and slugs

Usually the chemicals must be eaten by the pest to work. Baits are often used to attract and kill snails or slugs in an area.

## PETROCHEMICAL

- The prefix "petro-" is an arbitrary abbreviation of the word "petroleum";
- since "petro-" is Ancient Greek for "rock" and "oleum" means "oil". Therefore, the etymologically correct term would be "oleochemicals".
- However, the term oleochemical is used to describe chemicals derived from plant and animal fats.

**Explanation**

- Petrochemicals are chemical products derived from petroleum.
- Some chemical compounds made from petroleum are also obtained from other fossil fuels such as coal or natural gas, or renewable sources such as corn or sugar cane.



Petrochemical Plant in the Kingdom of Saudi Arabia

**Exercise Q3 (vi): Describe the basic building block in petrochemicals technology.**

### TYPES/CLASSES OF PETROCHEMICAL RAW MATERIALS (BUILDING BLOCKS):

Petrochemical classes are:-

(a) Olefins including ethylene and propylene.

(b) Aromatics

(c) Synthesis Gas

- Olefins and aromatics are the building blocks for a wide range of materials such as solvents, detergents, and adhesives.
- Primary petrochemicals are divided into three groups depending on their chemical structure:

#### (a) OLEFINS INCLUDING ETHYLENE AND PROPYLENE

- Olefins includes ethylene, propylene, and butadiene.
- At oil refineries olefins are produced mainly from hydrocarbons by chemical cracking such as steam cracking and by catalytic reforming.
- Ethylene and propylene are important sources of industrial chemicals and plastics products.
- Butadiene is used in making synthetic rubber.
- Olefins are the basis for polymers and oligomers used in plastics, resins, fibers, elastomers, lubricants, and gels.

#### (b) AROMATICS

- Aromatics includes benzene, toluene, and xylenes.
- At oil refineries, aromatic hydrocarbons are mainly produced by catalytic reforming or similar processes.
- Benzene is a raw material for dyes and synthetic detergents.
- Benzene and toluene are raw materials for isocyanates
- Manufacturers use xylenes to produce plastics and synthetic fibers.



### (c) SYNTHESIS GAS

- Synthesis gas is a mixture of carbon monoxide and hydrogen used to make ammonia and methanol.
- Ammonia is used to make the fertilizer urea and methanol is used as a solvent and chemical intermediate.
- A very wide range of chemicals and other materials is made from these basic building blocks. Which are used in industry monomers, solvents detergents, adhesives etc. f
- Form the monomers, polymer or oligomers of plastics, resins, fibres elastomers, certain lubricants and gels are produced.
- World is production of ethylene is around 110 million tons per annum of propylene 65 million tons and of aromatic raw materials 70 million tons.
- The largest petrochemicals industries are to be found in the USA and Western Europe, though the major growth in new production capacity is in the Middle East and Asia.
- There is a substantial inter-regional trade in petrochemicals of all kinds.

### LIST OF SIGNIFICANT PETROCHEMICALS AND THEIR DERIVATIVES

The following is a partial list of the major commercial petrochemicals and their derivatives:

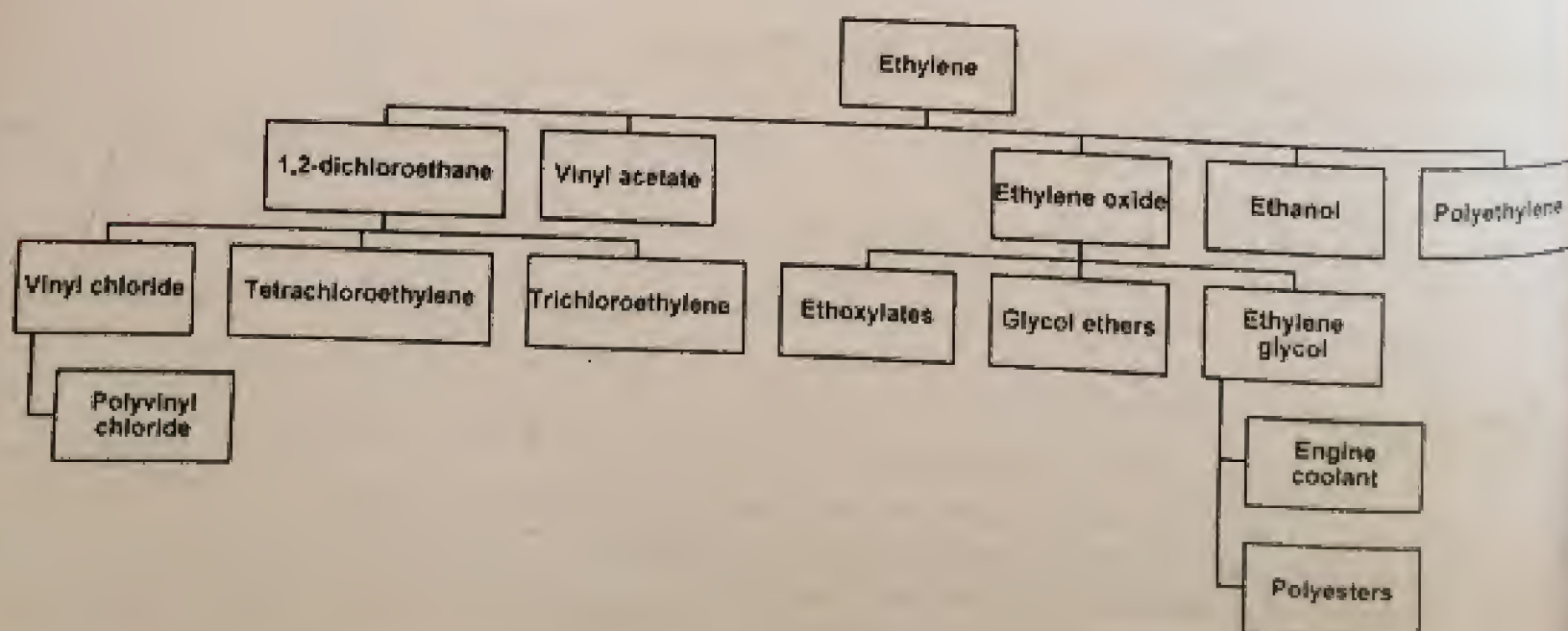
**Exercise Q2 (u) Enlist different chemicals produced from ethylene.**

#### CHEMICALS PRODUCED FROM ETHYLENE

**Ethylene:** The simplest olefin; used as a chemical feedstock and ripening hormone.

It is used to prepare following substances

- (i) **Polyethylene:** polymerized ethylene
- (ii) **Ethanol:** via ethylene hydration (chemical reaction adding water) of ethylene
- (iii) **Ethylene oxide:** via ethylene oxidation
  - (a) **Ethylene glycol:** via ethylene oxide hydration
    - Engine coolant: ethylene glycol, water and inhibitor mixture
    - Polyesters: any of several polymers with ester linkages in the backbone chain
  - (b) **Glycol ethers:** via glycol condensation
  - (c) **Ethoxylates:**
- (iv) **Vinyl acetate**
- (v) **1,2-dichloroethane**
  - (a) **Trichloroethylene**
  - (b) **Tetrachloroethylene:** also called perchloroethylene; used as a dry cleaning solvent and degreaser
  - (c) **Vinyl chloride:** monomer for polyvinyl chloride
    - Polyvinyl chloride (PVC):** type of plastic used for piping, tubing, other things

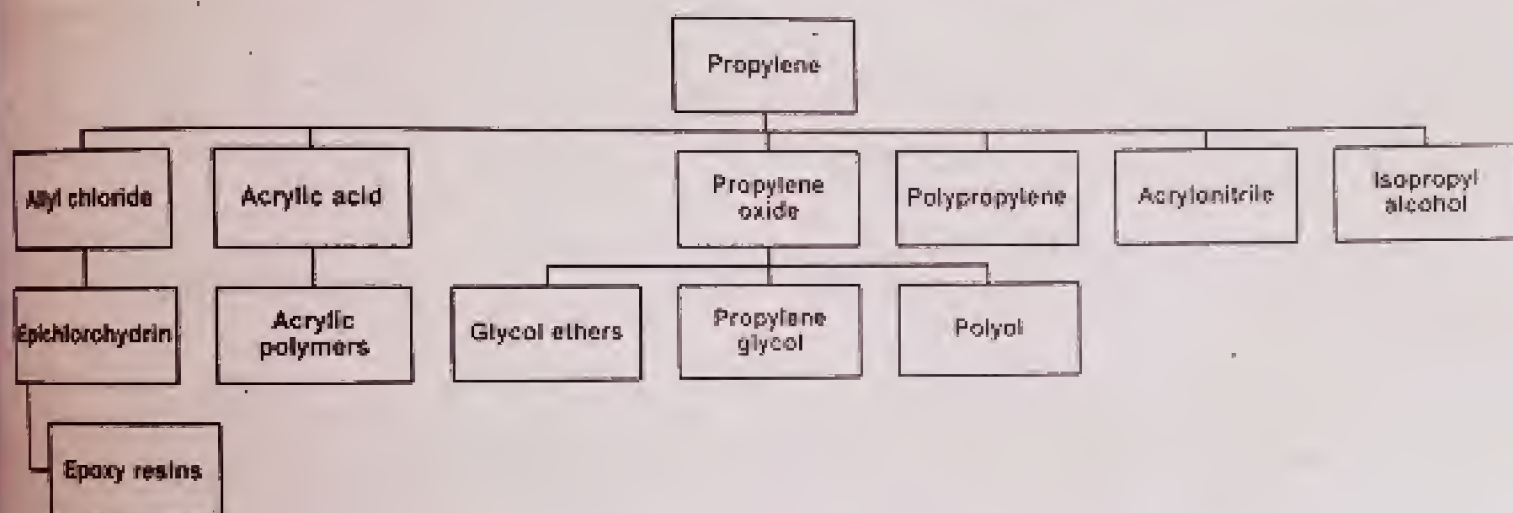




## CHEMICALS PRODUCED FROM PROPYLENE

**Propylene:** It is used as a monomer and a chemical feedstock. It is used to prepare following substances

- (i) isopropyl alcohol - 2-propanol; often used as a solvent or rubbing alcohol
  - (ii) acrylonitrile - useful as a monomer in forming Orlon, ABS
  - (iii) polypropylene - polymerized propylene
  - (iv) propylene oxide
    - (a) polyol - used in the production of polyurethanes
    - (b) propylene glycol - used in engine coolant and aircraft deicer fluid
    - (c) glycol ethers - from condensation of glycols
  - (v) acrylic acid: acrylic polymers
  - (vi) allyl chloride
    - (a) epichlorohydrin - chloro-oxirane; used in epoxy resin formation
- epoxy resins - a type of polymerizing glue from bisphenol A, epichlorohydrin, and some amine



## CHEMICALS PRODUCED FROM BENZENE

**Benzene** - the simplest aromatic hydrocarbon

- (i) **ethylbenzene** - made from benzene and ethylene
  - (a) styrene made by dehydrogenation of ethylbenzene; used as a monomer
  - polystyrenes - polymers with styrene as a monomer
- (ii) **cumene** - isopropylbenzene; a feedstock in the cumene process
  - (a) phenol - hydroxybenzene; often made by the cumene process
  - (b) acetone - dimethyl ketone; also often made by the cumene process
  - (c) bisphenol A - a type of "double" phenol used in polymerization in epoxy resins and making a common type of polycarbonate
    - epoxy resins - a type of polymerizing glue from
    - polycarbonate - a plastic polymer made from bisphenol A and phosgene (carbonyl dichloride)
  - (d) solvents - liquids used for dissolving materials; examples often made from petrochemicals include ethanol, isopropyl alcohol, acetone, benzene, toluene, xylenes
- (iii) **cyclohexane** - a 6-carbon aliphatic cyclic hydrocarbon sometimes used as a non-polar solvent
  - (a) adipic acid - a 6-carbon dicarboxylic acid which can be a precursor used as a co-monomer together with a diamine to form an alternating copolymer form of nylon.
  - (b) caprolactam - a 6-carbon cyclic amide
    - nylons - types of polyamides, some are alternating copolymers formed from copolymerizing dicarboxylic acid or derivatives with diamines. Some are from polymerizing caprolactam



(iv) **nitrobenzene** - can be made by single nitration of benzene

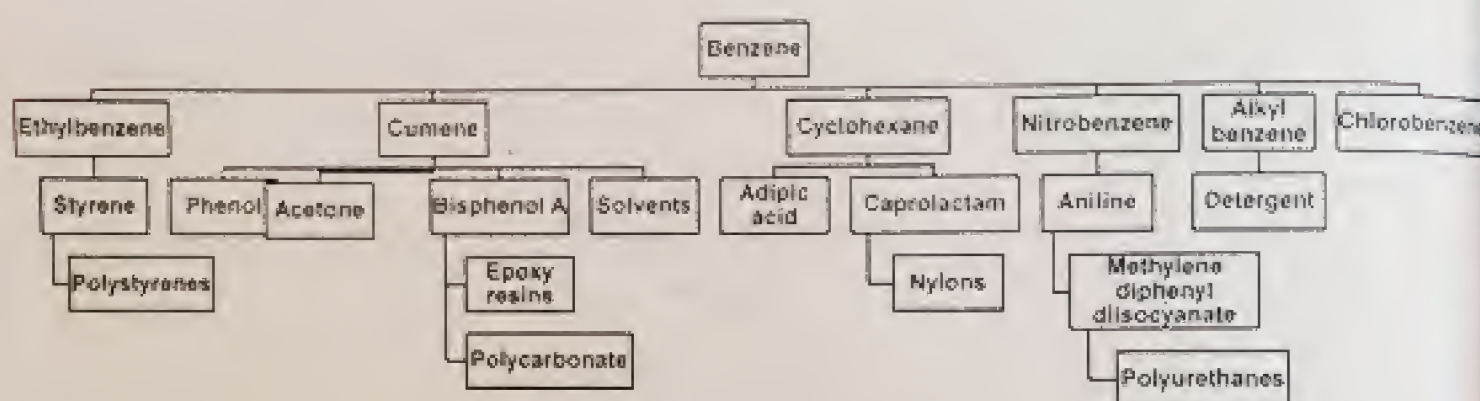
(a) aniline - aminobenzene

- methylene diphenyl diisocyanate (MDI) - used as a co-monomer with diols or polyols to form polyurethanes or with di- or polyamines to form polyureas.
- polyurethanes

(v) **alkylbenzene** - a general type of aromatic hydrocarbon which can be used as a precursor for a sulfonate surfactant (detergent)

(a) detergents - often include surfactants types such as alkylbenzenesulfonates and nonylphenol ethoxylates

(vi) **chlorobenzene**



**Exercise Q2 (vi) Enlist different chemicals produced from ethylene.**

### CHEMICALS PRODUCED FROM TOLUENE

**Toluene:** methylbenzene; can be a solvent or precursor for other chemicals

(i) **benzene:**

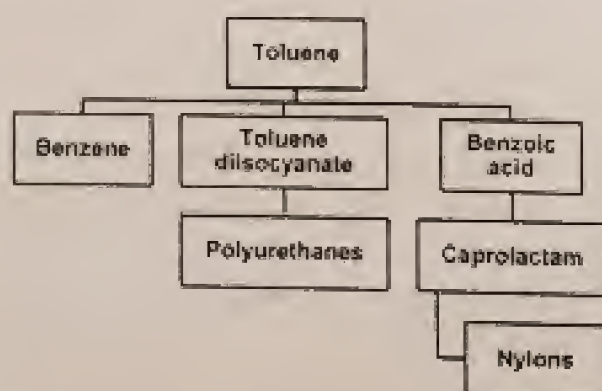
(ii) **Toluene diisocyanate (TDI):** used as co-monomers with diols or polyols to form polyurethanes or with di- or polyamines to form polyureas

(a) polyurethanes - a polymer formed from diisocyanates and diols or polyols

(iii) **benzoic acid** - carboxybenzene

(a) caprolactam

- Nylons



### Chemicals produced from xylenes

**Mixed xylenes** - any of three dimethylbenzene isomers, could be a solvent but more often precursor chemicals

(i) **ortho-xylene** - both methyl groups can be oxidized to form (ortho-)phthalic acid

(a) phthalic anhydride



(ii) **meta-xylene**

(a) isophthalic acid

- alkyd resins
- Polyamide Resins
- Unsaturated Polyesters

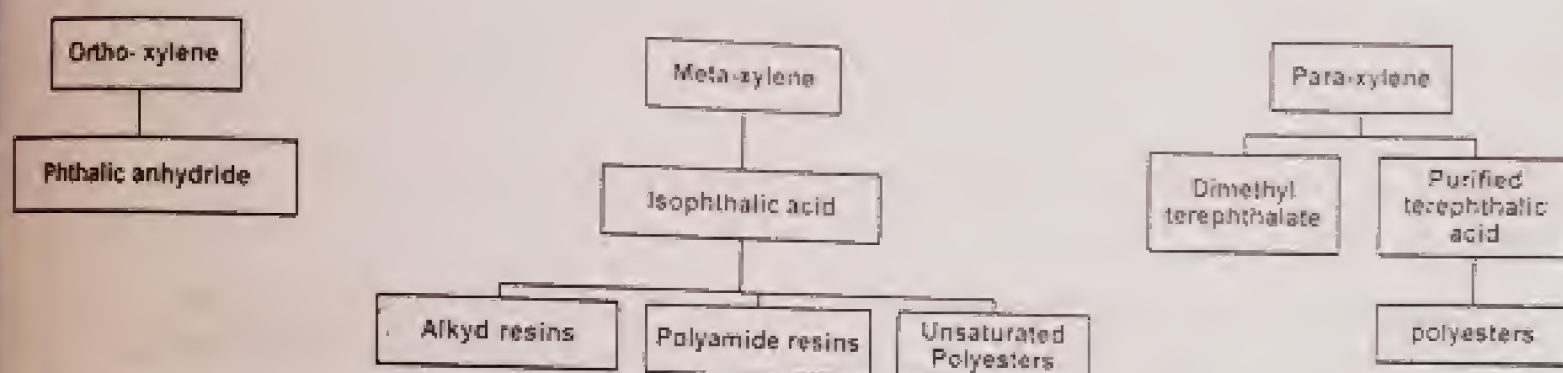
(iii) **para-xylene** - both methyl groups can be oxidized to form terephthalic acid

(a) dimethyl terephthalate - can be copolymerized to form certain polyesters

- polyesters: although there can be many types, polyethylene terephthalate is made from petrochemical products and is very widely used.

(b) purified terephthalic acid - often copolymerized to form polyethylene terephthalate

- polyesters



## QUICK QUIZ-5

(1) **What do you mean by petrochemicals**

Petrochemicals are chemical products derived from petroleum.

Three important classes of petrochemicals are:

- Olefins including ethylene and propylene, e.g. ethylene, propylene, and butadiene.
- Aromatics e.g. benzene, toluene, and xylenes.
- Synthesis Gas e.g. a mixture of carbon monoxide and hydrogen used to make ammonia and methanol

(2) **What are classes of petrochemical raw materials**

Three important classes of petrochemicals are:

- Olefins including ethylene and propylene, e.g. ethylene, propylene, and butadiene.
- Aromatics e.g. benzene, toluene, and xylenes.
- Synthesis Gas e.g. a mixture of carbon monoxide and hydrogen used to make ammonia and methanol

(3) **What are important fractions of petroleum**

Important fractions of petroleum are:

Petroleum gas, Gasoline (Petrol), Naphtha, Kerosene oil, Diesel oil, Lubrication oil, Fuel oil and Bitumen.

(4) **How does refining of petroleum carried out in Pakistan.**

- The oil obtained from the oil fields of Dhulian, Khaur, Balkasar and Joyameer is refined by Pakistan Oil Fields Limited near Rawalpindi. The imported crude oil is refined at Karachi.

- The main refineries of Pakistan are:

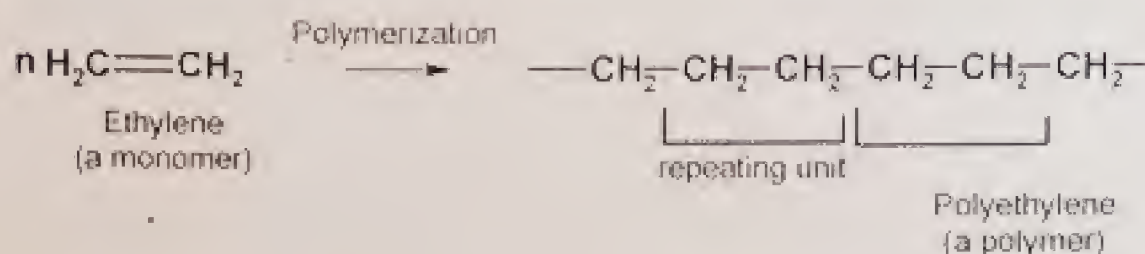
- Attock oil refinery
- Pakistan oil refinery
- National oil refinery
- Pak-Arab refinery



## SYNTHETIC POLYMERS

- Polymers are high molecular weight compounds whose structures are made up of a large number of simple repeating units.
- The repeating units are usually obtained from low molecular weight simple compounds called as monomers.
- The reaction by which monomers are converted into polymers is known as polymerization.

### Example



The formation of polyethylene from ethylene is an example of polymerization reaction.

- Polymers which are synthesized from only one kind of monomer are called **homopolymers**.
- Polymers which are prepared from more than one kind of monomer are called **copolymers**.

## CLASSIFICATION OF POLYMERS

There are two main types of polymers: Addition polymers and Condensation polymers.

### (I) ADDITION POLYMERS (CHAIN-GROWTH POLYMERS)

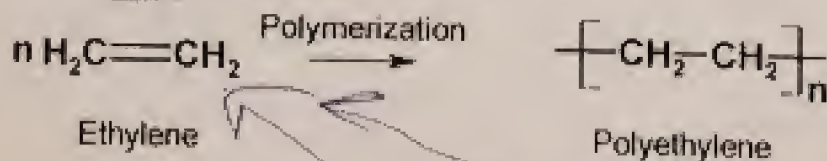
Addition polymers are formed by combination of alkenes monomers to produce a single huge molecule only.

- These reactions are catalyzed by peroxides or acids.
- The reactions require pressures of 1000 atmospheres at 2000°C.
- Much lower temperatures and pressures can be used with so called **Ziegler Catalysts** which consist of a trialkyl aluminum and titanium tetrachloride in an inert solvent.

#### (a) POLYETHYLENE (POLYTHENE)

- Polyethylene has been produced commercially since 1943.
- It is obtained by polymerizing ethylene.

In chain growth polymerization, the monomers are added at one end of growing chain.



- Notice that the monomer (ethylene) contains a double bond and the polymer does not.
- The electrons of the monomer pi bond have moved and are used to link one monomer unit to another by sigma bonds as indicated by extended lines in abbreviated polymer formula.
- The backbone of the polymer consists of the carbon atoms that originally formed the double bonds.
- Nothing is lost. The monomers simply add to each other.

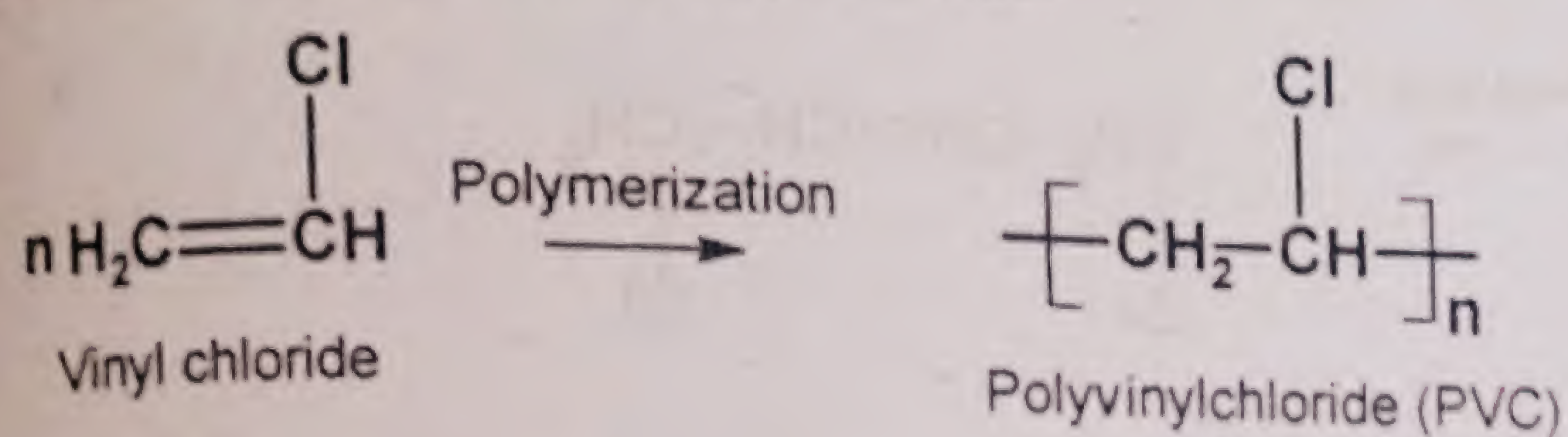
### Uses

It is used in the manufacture of houseware such as buckets and dustbins, carpet backing, packing materials, and cable insulation.

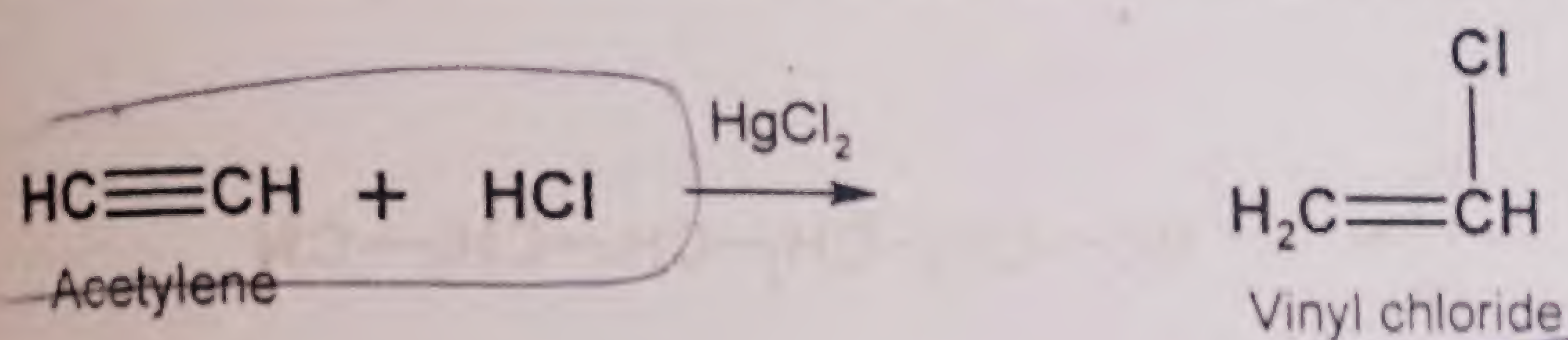


## POLYVINYL CHLORIDE (PVC)

It is obtained by polymerizing vinyl chloride.



Vinyl chloride is obtained from acetylene by treatment with HCl in the presence of  $\text{HgCl}_2$



### Uses

PVC is used in the manufacture of imitation leather, floor covering, corrugated roofing material and gramophone records.

## (ii) CONDENSATION POLYMERS (STEP-GROWTH POLYMERS)

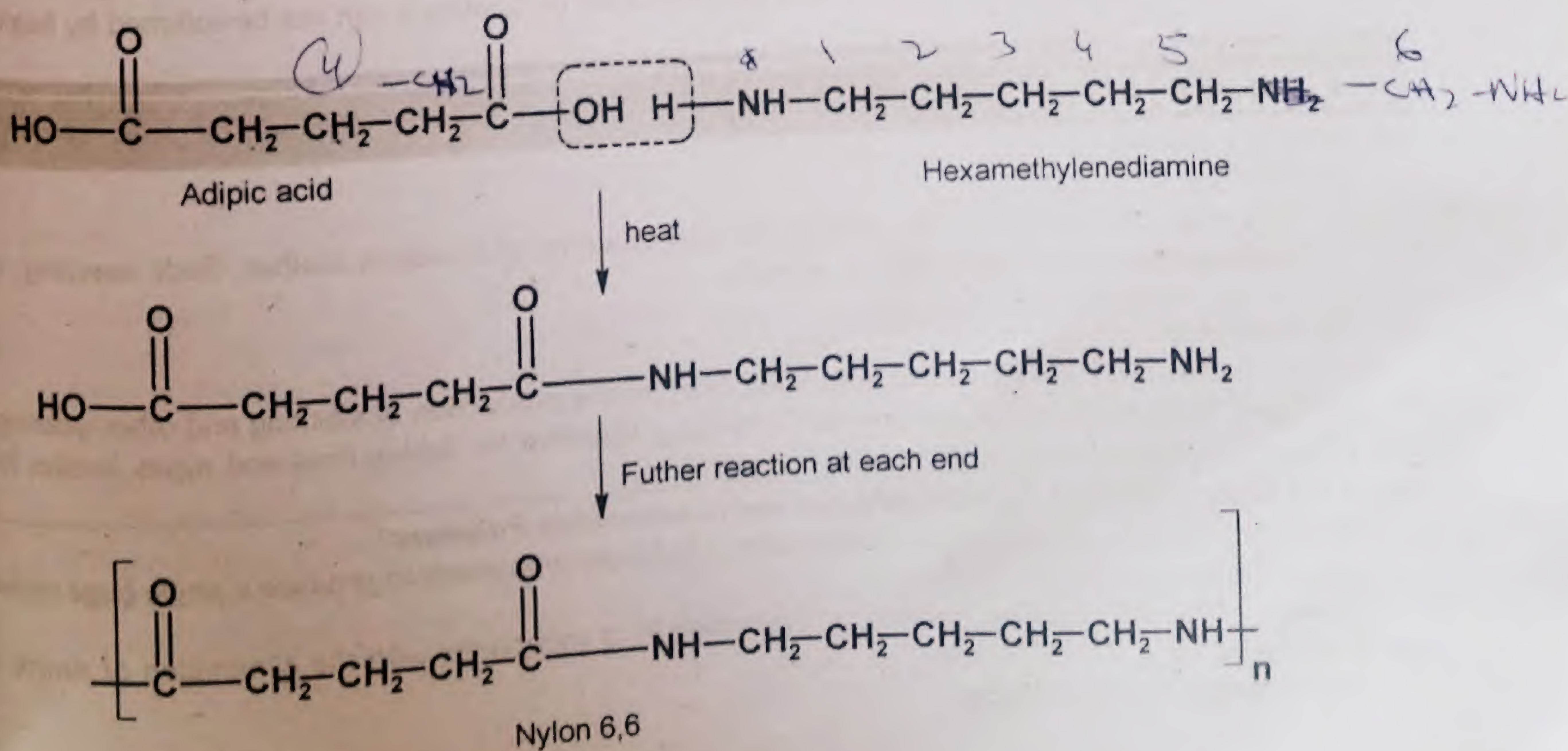
Condensation polymers are formed by combination of monomers with the elimination of simple molecules such as  $\text{H}_2\text{O}$  or  $\text{CH}_3\text{OH}$ .

There are two main types of condensation polymers: Polyesters or Polyamides. The most common example is:

### Nylon-6,6

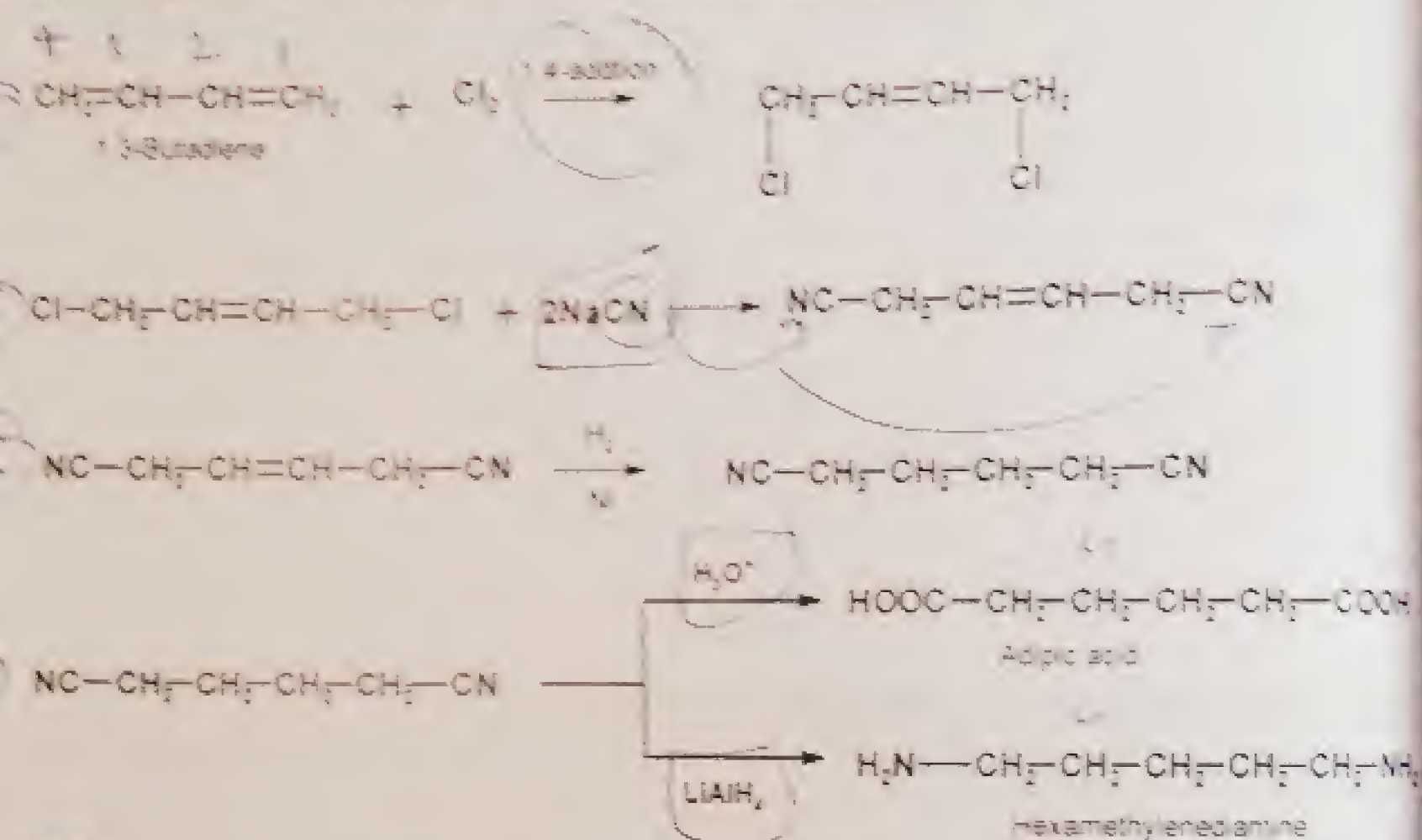
In step-growth polymerization, first bifunctional compounds react together to form dimer, trimer, tetramer etc. and finally at the end all these units together to form a polymer.

- It is the most important polyamide.
- It is obtained by heating adipic acid with hexamethylene diamine under nitrogen at  $200^\circ\text{C}$ .
- Nylon-6,6 derives its name from its starting materials, adipic acid and hexamethylene diamine, both of which have six carbons.





Both starting materials can be prepared from 1,3-butadiene as shown below:



#### Uses

- Nylon-6,6 was developed as a synthetic fiber for the production of stocking and other wearing apparel. It was introduced to the public at the New York World's Fair in 1939.
- It is used to make fibers for clothing and carpeting, filaments for fishing lines and ropes, bristles for brushes, and molded objects such as gears and bearings.

### THERMOPLASTIC AND THERMOSETTING POLYMERS

- A thermoplastic polymer is one which softens on heating and becomes hard on cooling.
- A thermosetting polymer is one which becomes hard on heating it can not be softened by heating.

### QUICK QUIZ-6

- What are uses of
- PVC

Poly(vinyl chloride) (PVC) is used in the manufacture of imitation leather, floor covering, corrugated roofing material and gramophone records.

- Nylon-6,6

- Nylon-6,6 is developed as a synthetic fiber for the production of stocking and other wearing apparel.
- It is used to make fibers for clothing and carpeting, filaments for fishing lines and ropes, bristles for brushes, and molded objects such as gears and bearings.

- What is the difference between addition and condensation Polymers?

Addition polymers are formed by combination of alkenes monomers to produce a single huge molecule only.  
e.g. polyethylene

Condensation polymers are formed by combination of monomers with the elimination of simple molecules such as  $\text{H}_2\text{O}$  or  $\text{CH}_3\text{OH}$ .  
e.g. Polyesters or Polyamides.

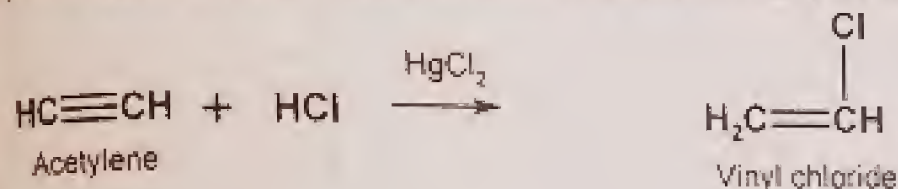


Q. Give difference between thermoplastic and thermosetting plastic

- A thermoplastic polymer is one which softens on heating and becomes hard on cooling. e.g. Polyvinyl chloride (PVC)
- A thermosetting polymer is one which becomes hard on heating it cannot be softened by heating. e.g., Bakelite.

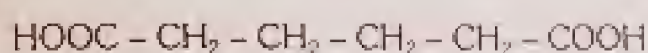
Q. How vinyl chloride is prepared from acetylene

Vinyl chloride is obtained from acetylene by treatment with HCl in the presence of  $\text{HgCl}_2$ .

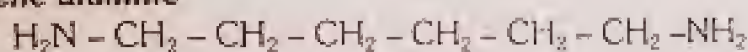


Q. Write formula of

(i) adipic acid



(ii) hexamethylene diamine



Q. Give use of Nylon-6,6

- Nylon-6,6 is developed as a synthetic fiber for the production of stocking and other wearing apparel.
- It is used to make fibers for clothing and carpeting, filaments for fishing lines and ropes, bristles for brushes, and molded objects such as gears and bearings.

## SOCIETY, TECHNOLOGY AND SCIENCE

### DEVELOPMENT OF SYNTHETIC FIBERS

- Nylon is the first synthetic fiber.
- Synthetic fibers are made from synthesized polymers or small molecules.
- The compounds that are used to make these fibers come from raw materials such as petroleum based chemicals or petrochemicals. These materials are polymerized into a long, linear chemical that bond two adjacent carbon atoms.
- Different chemical compounds will be used to produce different types of fibers.

**Manufacturing of Synthetic Fibers: Melt-Spinning Process.**

- There are several methods of manufacturing synthetic fibers but the most common is the **Melt-Spinning Process**.
  - ✓ It involves heating the fiber until it begins to melt, then drawing out the molten fiber with tweezers as quickly as possible.
  - ✓ The next step is to draw the molecules by aligning them in a parallel arrangement. This brings the fibers closer together and allows them to crystallize and orient.
  - ✓ Lastly, is Heat-Setting. This utilizes heat to permeate the shape and dimensions of the fabrics made from heat-sensitive fibers.
- In general, synthetic fibers are created by forcing, usually through extrusion (the act or process of pushing or thrusting out to create objects of a fixed, cross-sectional profile) fiber, forming materials through holes (called spinnerets) into the air, forming a thread.
- Before synthetic fibers were developed, artificially manufactured fibers were made from cellulose.



## USES OF SYNTHETIC FIBRES

Synthetic fibres are used for making

- Clothes
- Ropes
- Nylon is used in making stockings, parachutes and other military equipment.
- Fish nets
- Carpets
- Tents
- Dacron is used in making rugs
- **Glass fiber** is used for:
  - ✓ industrial, automotive and home insulation (glass wool)
  - ✓ reinforcement of composite materials (glass reinforced plastic, glass fiber reinforced concrete)
  - ✓ specialty papers in battery separators and filtration
- **Metallic fiber** is used for:
  - ✓ adding metallic properties to clothing for the purpose of fashion (usually made with composite plastic and metal foils)
  - ✓ elimination and prevention of static charge build-up
  - ✓ conducting electricity to transmit information
  - ✓ conduction of heat
- **In the horticulture industry** synthetics are often used in soils to help the plants grow better. e.g.
  - ✓ expanded polystyrene flakes
  - ✓ urea-formaldehyde foam resin
  - ✓ polyurethane foam
  - ✓ phenolic resin foam.

## COSMETIC CHEMISTRY

### Introduction

- The global market for skincare and color cosmetics exceeded 53 billion dollars in 2002.
- The number of new products brought to market continues to expand exponentially.
- Cosmetic chemists are always looking for interesting and exotic ingredients that improve skin's appearance and health.
- A vast array of compounds is required to supply these products.
- The latest edition of the Cosmetics Toiletries and Fragrance Association (CTFA) Dictionary lists more than 10,000 raw materials.
- Every year hundreds of new ingredients are added to the list of those that have been used for centuries.

Following are the important cosmetics

- (1) Nail Polish
- (2) Nail Polish Remover
- (3) Lipstick
- (4) Hair dyes

## NAIL POLISH

### BACKGROUND

- Nail polish (or lacquer, or enamel) is almost completely an invention of twentieth century technology. However, other cosmetics have a history of hundreds or even thousands of years.



- Nail coverings were not unknown in ancient times. The upper classes of ancient Egypt probably used henna to dye both hair and fingernails. Essentially, as composition, manufacture and handling reflect developments in modern chemical technology.
- Modern nail polish is sold in liquid form in small bottles and is applied with a tiny brush.
- Within a few minutes after application, the substance hardens and forms a shiny coating on the fingernail. This coating is both water- and chip-resistant.
- Generally, a coating of nail polish may last several days before it begins to chip and fall off.
- Nail polish can also be removed manually by applying nail polish "remover". It is a substance designed to break down and dissolve the polish.

**Exercise Q3 (vii): Describe raw materials and manufacturing process of Nail Polish.**

### RAW MATERIALS

There is no single formula for nail polish. There are, however, a number of ingredient types that are used. These basic components include:

- (1) **Film forming agents** e.g. Nitrocellulose
- (2) **Resins and plasticizers** e.g. castor oil, amyl and butyl stearate, and mixes of glycerol, fatty acids, and acetic acids
- (3) **Solvents** e.g. Butyl stearate and acetate compounds
- (4) **Coloring agents** e.g. "pearl" or "fish scale"

### THE MANUFACTURING PROCESS

Includes following steps:

- (1) When properly and fully milled, the mixture is removed from the mill in sheet form and then broken up into small chips for mixing with the solvent. The mixing is performed in **stainless steel** kettles.

**Caution:**

This step is performed in a special room or area designed to control the hazards of fire and explosion. Most modern factories perform this step in an area with walls that will close in if an alarm sounds and, in the event of explosion, with ceilings that will safely blow off without endangering the rest of the structure.

- (2) At the end of the process, the mix is cooled slightly before the addition of such other materials as perfumes and moisturizers.

- (3) The mixture is then pumped into smaller, 55 gallon drums, and then trucked to a production line. The finished nail polish is pumped into explosion proof pumps, and then into smaller bottles suitable for the retail market.

### NAIL POLISH REMOVER

Nail polish remover base commonly contains a mixture of two organic solvents **acetone** and **ethyl acetate**.

- **Acetone** belongs to a group of organic molecules called ketones or alkanones. The proper name acetone is propanone. It is also sometimes called 2-propanone.
- **Ethyl acetate** belongs to a group of organic molecules called esters or alkyl alkanoates. The proper name for ethyl acetate is ethyl ethanoate.

### Interesting Information

Acetone is an organic liquid that is colorless, flammable and is often used as a solvent as it is completely miscible with water and nearly all other organic liquids.

### QUICK QUIZ-7

- (1) Give composition of nail polish

The basic components include:

- (i) **Film forming agents** e.g. Nitrocellulose



- (ii) Resins and plasticizers e.g. castor oil, amyl and butyl stearate and mixture of glycerol, amyl, lauryl and acetyl acids
- (iii) Solvents e.g. Butyl stearate and acetate compounds
- (iv) Coloring agents e.g. "pearl" or "fish scale"

(2) What is use of plasticizers in nail polish?

The function of all plasticizers is to produce elasticity in the product.

(3) In which material mixing of raw material of nail polish is preferred?

The mixing is performed in stainless steel kettles.

(4) What is nail polish remover?

Nail polish can also be removed manually by applying nail polish "remover". It is a substance designed to break down and dissolve the polish.

Nail polish remover base commonly contains a mixture of two organic solvents acetone and ethyl acetate.

(5) Give composition of nail polish remover

Nail polish remover base commonly contains a mixture of two organic solvents acetone and ethyl acetate.

- Acetone belongs to a group of organic molecules called ketones or alkanones.
- Ethyl acetate belongs to a group of organic molecules called esters.

## LIPSTICK AND CHEMICAL COMPOSITION

- Lipsticks are simple in chemical composition, however complicated their application or effects.
- They are made up of three ingredients—a waxy or fatty base, a dye and a perfume.
- There is no danger in the use of lipstick. In fact, for sensitive mucous membranes they are protective.
- Anyone can eat a lipstick with no more harm than eating a pat of butter.

## RAW MATERIALS AND COMPOSITION

The primary ingredients found in lipstick are:

- (i) Wax (The wax used usually involves some combination of three types: beeswax, candelilla wax, or the more expensive carnauba wax)
- (ii) Oil (such as mineral, castor, lanolin, or vegetable oil)
- (iii) Alcohol,
- (iv) Fragrance and pigment,
- (v) Preservatives and antioxidants.

Generally, the composition by weight is

- Wax and oil make up about 60 percent of the lipstick.
- Alcohol and pigment make up 25 percent.
- Fragrance added to lipstick, make up 1% or less of the mixture.

## THE MANUFACTURING PROCESS

The manufacturing process comprises of three separate steps:

- (i) melting and mixing the lipstick
- (ii) pouring the mixture into the tube
- (iii) packaging the product for sale.



### Melting and Mixing

- First, the raw ingredients for the lipstick are melted and mixed separately. It is because of the different types of ingredients used. So, three mixtures are prepared separately.
  - One contains the solvents.
  - Second contains the oils.
  - Third contains the fats and waxy materials.
- The solvent solution and liquid oils are then mixed with the color pigments.
- After the pigment mass is ground and mixed, it is added to the hot wax mass until a uniform color and consistency is obtained.

### Molding

- Once the lipstick mass is mixed and free of air, it is ready to be poured into the tube.
- A variety of machine setups are used, depending on the equipment that the manufacturer has.
- The melted mass is dispensed into a mold, "up-side down" so that the bottom of the tube is at the top of the mold.
- The lipstick is cooled and separated from the mold, and the bottom of the tube is sealed.
- The lipstick then passes through a flaming cabinet (or is flamed by hand) to seal pinholes and improve the finish.

### Labelling and Packaging

- After the lipstick is retracted and the tube is capped, the lipstick is ready for labelling and packaging.
- Labels identify the batch and are applied as part of the automated operation.
- The final step in the manufacturing process is the packaging of the lipstick tube. There are a variety of packaging options available.

## QUICK QUIZ-8

### 1) Give composition of lipstick

Generally, the composition by weight is

- Wax and oil make up about 60 percent of the lipstick.
- Alcohol and pigment make up 25 percent.
- Fragrance added to lipstick, make up 1% or less of the mixture.

### 2) What type of wax is used as raw material of lipstick

The wax used usually involves some combination of three types: beeswax, candelilla wax, or the more expensive carnauba wax.

### 3) How many steps are involved in manufacturing of lipstick

The manufacturing process comprises of three separate steps:

- melting and mixing the lipstick
- pouring the mixture into the tube
- packaging the product for sale.

### 4) Give percentage of alcohol and pigments in lipstick

Alcohol and pigment make up 25 percent by weight of the lipstick.



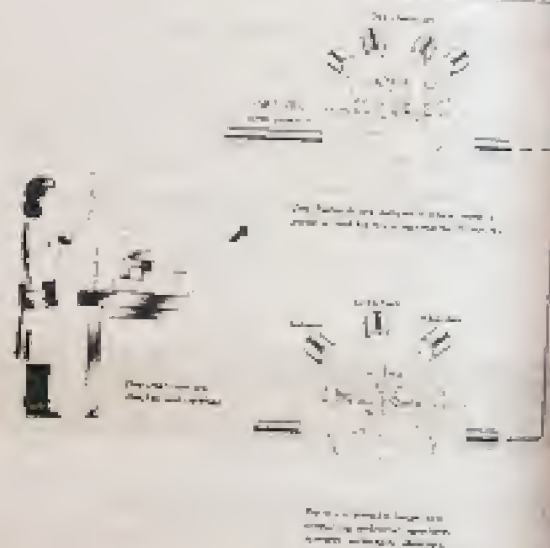
## HAIR DYE

### HISTORY:

1. Hair dye is one of the oldest known beauty preparations, and was used by ancient cultures in many parts of the world. Records of ancient Egyptians, Greeks, Hebrews, Persians, Chinese, and early Hindu peoples all mention the use of hair colorings.
2. Early hair dyes were made from plants, metallic compounds, or a mixture of the two.
3. Rock alum, quicklime, and wood ash were used for bleaching hair in Roman times. Henna was known in many parts of the world; it produces a reddish dye.
4. Many different plant extracts were used for hair dye in Europe and Asia before the advent of modern dyes.
5. Indigo, known primarily as a fabric dye, could be combined with henna to make light brown to black shades of hair dye.
6. An extract of the flowers of the chamomile plant was long used to lighten hair, and this is still used in many modern hair preparations.
7. The bark, leaves, or nutshells of many trees were used for hair dyes.
8. Other dyes were produced from walnut leaves or nut husks.

### MODERN AGE:

- Preparations such as these were the only hair dyes available until the late nineteenth century.
- Hydrogen peroxide was discovered in 1818, but it was not until 1867 that it was exhibited at the Paris Exposition as an effective hair lightener.
- A London chemist and a Parisian hairdresser began marketing a 3% hydrogen peroxide formula at the Exposition as *eau de fontaine de jeunesse* golden (golden fountain of youth water). This was the first modern chemical hair colorant.
- Advances in chemistry led to the production of more hair dyes in the late nineteenth century.
- The first synthetic organic hair dye developed was pyrogallol, a substance that occurs naturally in walnut shells.



### RAW MATERIALS

- In general, hair dyes include:
  - (i) **Dyes** e.g. 4-amino-2-hydroxytoluene
  - (ii) **Modifiers** e.g. resorcinol
  - (iii) **Antioxidants** e.g. sodium sulfite
  - (iv) **Alkalizers** e.g. ammonium hydroxide
- In addition to these basic chemicals, many different chemicals are used to impart special qualities. They may be shampoos, fragrances, chemicals that make the formula creamy, foamy, or thick, or contribute to the overall action of the formula.
- Hair dyes are usually packaged with a developer, which is in a separate bottle.
- The developer is most often based on hydrogen peroxide, with the addition of small amounts of other chemicals depending on the manufacturer.

### THE MANUFACTURING PROCESS

- The manufacturing process includes the following steps
- First of all chemicals must be tested to make sure they are what they are labeled. Then weigh the chemicals accurately.



Further these chemicals are mixed in preheated water other solvents. The premix is agitated for about 20 minutes.

The pre mix is then added to a large tank, containing the other ingredients of the hair dye.

After getting proper consistency this mixture is delivered to a tank where it is filled in bottles labeled caped, pack with developer and then distributed in the market.

**Exercise Q3 (viii):** What are adhesives? Discuss its working and types.

## ADHESIVES

**An adhesive is a compound that adheres or bonds two items together.**

- Adhesives are meant to stick things together.
- Adhesives may come from either natural or synthetic sources. i.e. Adhesives are nature product and it is also manufactured in Factories.
- Some modern adhesives are extremely strong, and are becoming increasingly important in modern construction and industry.

### TYPES OF ADHESIVES:

#### (1) NATURAL ADHESIVES:

- These are made from inorganic mineral sources, or biological sources such as vegetable matter, starch (dextrin), natural resins, animal skin.
- They are often referred to as bioadhesives.

#### (2) SYNTHETIC ADHESIVES:

Elastomers, thermoplastic, and thermosetting adhesives are examples of synthetic adhesives.

#### (3) DRYING ADHESIVES:

The drying adhesives are a combination of ingredients suspended in a solvent. As the solvent evaporates, the adhesive hardens. e.g. White glue and rubber cements.

#### (4) CONTACT ADHESIVES:

- Contact adhesives must be applied to both surfaces and allowed some time to dry before the two surfaces are pushed together.
- Some contact adhesives require as long as 24 hours to dry before the surfaces are to be held together.

#### (5) HOT GLUE:

- It is also known as "hot melt" adhesives.
- These adhesives are thermoplastics.
- They are applied hot and simply allowed to harden as they cool.
- These adhesives have become popular for crafts because of their ease of use and the wide range of common materials to which they can adhere.
- The glue gun melts the solid adhesive and then allows the liquid to pass through the "barrel" of the gun onto the material where it solidifies.

#### (6) UV AND LIGHT CURING ADHESIVES:

UV and light curing adhesives consist essentially of low or medium molecular weight resins.



## QUICK QUIZ-8

**(1) Define adhesives**

An adhesive is a compound that adheres or bonds two items together. Adhesives are meant to stick things together.

**(2) Give few examples of natural adhesives**

These are made from inorganic mineral sources, or biological sources such as vegetable matter (starch, dextrin), natural resins, animal skin. They are often called as bioadhesives.

**(3) Why and when drying adhesives harden**

The drying adhesives are a combination of ingredients suspended in a solvent. As the solvent evaporates, the adhesive hardens. e.g. White glue and rubber cements.

**(4) How adhesives are used applied**

- The drying adhesives are a combination of ingredients suspended in a solvent. As the solvent evaporates, the adhesive hardens. e.g. White glue and rubber cements.
- The contact adhesives must be applied to both surfaces and allowed some time to dry before the two surfaces are pushed together.

**(5) How hot glue is applied?**

Hot glue is applied hot and allowed to harden as they cool.

**(6) Low molecular resins are present in which category or adhesive.**

UV and light curing adhesives consist essentially of low or medium molecular weight resins.

## KEY POINTS

- Classical chemistry (organic, inorganic and physical chemistry) is very essential for advancing the science of chemistry by discovering and reporting new products, routes and techniques.
- Capital-intensive industries are classified as heavy while labour intensive industries are classified as light industries.
- Light industries are easier to relocate than heavy industries and require less capital investment to build.
- Specialty chemicals are mainly used in the form of formulations. Purity is of vital importance in their formulation. This calls for organic synthesis of highly valued pure chemicals known as fine chemicals.
- The polar auxochrome makes the dye water-soluble and binds the dye to the fabric by interaction with the oppositely charged groups of the fabric structure.
- Insecticides, fungicides, herbicides, etc., are all types of pesticides. Some pesticides must only contact (touch) the pest to be deadly. Others must be swallowed to be effective.
- Petrochemicals are chemical products derived from petroleum. Some chemical compounds made from petroleum are also obtained from other fossil fuels such as coal or natural gas, or renewable sources such as corn or sugar cane.
- Polymers which are synthesized from only one kind of monomer are called homopolymers. Polymers which are prepared from more than one kind of monomer are called copolymers.**
- A thermoplastic polymer is one which softens on heating and becomes hard on cooling.
- A thermosetting polymer is one which becomes hard on heating it can not be softened by heating.
- Modern nail polish is sold in liquid form in small bottles and is applied with a tiny brush.
- Nail polish remover base commonly contains a mixture of two organic solvents acetone and ethyl acetate.
- Lipsticks are simple in chemical composition, however complicated their application or effects. They are made up of three ingredients—a waxy or fatty base, a dye and a perfume.
- Many different plant extracts were used for hair dye in Europe and Asia before the advent of modern dyes.
- Elastomers, thermoplastic, and thermosetting adhesives are examples of synthetic adhesives.



## EXERCISE

**Q1: Select the right answer from the choices given with each question.**

- (i) The branch of chemistry which applies physical and chemical procedures towards the transformation of natural raw material and their derivatives to products is called:
  - (a) physical chemistry (b) classical chemistry (c) industrial chemistry (d) both b and c
- (ii) Which dye is used in boot polish
  - (a) Azo dye (b) Congo red (c) Methyl orange (d) Bismarck Brown
- (iii) Miticides are used to control
  - (a) ticks and mites (b) Fungi (c) Unwanted plants (d) mice and bats
- (iv) Aerosoles and lotions are used as
  - (a) Fungicides (b) Repellent (c) Herbicides (d) a and c
- (v) Petrochemicals are classified into how many classes?
  - (a) One (b) Two (c) Three (d) Four
- (vi) How many classes of polymers?
  - (a) One (b) Two (c) Three (d) Four
- (vii) Nylon is a polymer obtained by
  - (a) Addition polymerization (b) Condensation polymerization (c) Homopolymer (d) None
- (viii) Which of following is not a raw material for nail polish?
  - (a) Pearl (b) Castor oil (c) Resorcinol (d) Nitrocellulose
- (ix) A polymer which becomes hard on heating is:
  - (a) Thermosetting (b) Thermoplastic (c) Addition (d) None
- (x) Nail Polish remover base commonly contains a mixture of two organic solvents as
  - (a) Benzene and acetone (b) ethyl acetate and  $CS_2$  (c) Benzene and  $CS_2$  (d) acetone and ethyl acetate
- (xi) Which of following adhesives are also known as bioadhesives?
  - (a) Drying adhesives (b) Synthetic adhesives (c) Natural adhesives (d) Hot glue
- (xii) A chemical compounds which is meant to stick things together
  - (a) Nail polish (b) Lipstick (c) Hair dye (d) adhesives
- (xiii) In early ages hair dyes were made from
  - (a) plants (b) animals (c) metallic compounds (d) both a and c
- (xiv) Polymers which are prepared from more than one kind of monomer are
  - (a) homopolymer (b) copolymer (c) addition polymer (d) none

## ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (c) industrial chemistry By definition it is industrial chemistry	(ii) Ans: (d) Bismarck Brown Bismarck Brown is used in boot polish
(iii) Ans: (a) ticks and mites The chemicals which kills mites are called miticides	(iv) Ans: (b) Repellent Aerosoles and lotions are repellent
(v) Ans: (c) Three The three classes of petrochemicals are: olefins, aromatics and synthesis gas.	(vi) Ans: (b) Two There are two main types of polymers: Addition polymers and Condensation polymers.
(vii) Ans: (b) Condensation polymerization Nylon is polyamide. It is obtained by condensation of adipic acid and hexamethylene diamine with the loss of water.	(viii) Ans: (c) Resorcinol The raw materials for nail polish are Pearl, Castor oil and Nitrocellulose
(ix) Ans: (a) Thermosetting By definition it is thermosetting	(x) Ans: (d) acetone and ethyl acetate Nail polish remover has base of two solvents: acetone and ethyl acetate.
(xi) Ans: (c) Natural adhesives Natural adhesives are obtained from living organisms i.e. plants. So they are called natural adhesives	(xii) Ans: (d) adhesives Adhesives bind or stick things together.
(xiii) Ans: (d) both a and c Early hair dyes were made from plants, metallic compounds, or a mixture of the two.	(xiv) Ans: (b) copolymer Polymers made from two kind of monomers are called copolymers



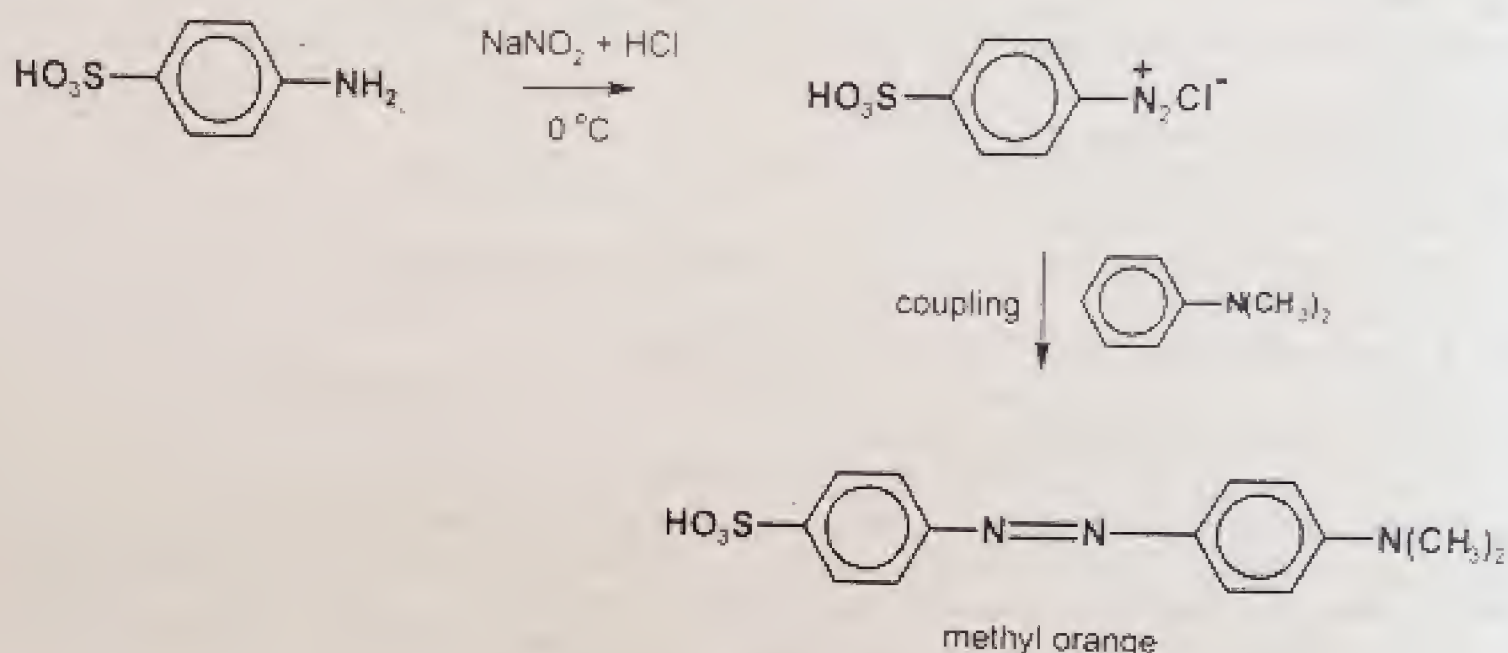
**Q2: Give brief answers for the following questions.**

(i) What is the difference between classical and industrial chemistry.

- The Classical Chemistry (organic, inorganic and physical chemistry) is very essential for advancing science of chemistry. It discovers and reports new products, routes and techniques.
- The industrial chemistry applies physical and chemical procedures, discovered by classical chemistry, towards the transformation of natural raw materials and their derivatives to products that are of benefit to humanity.

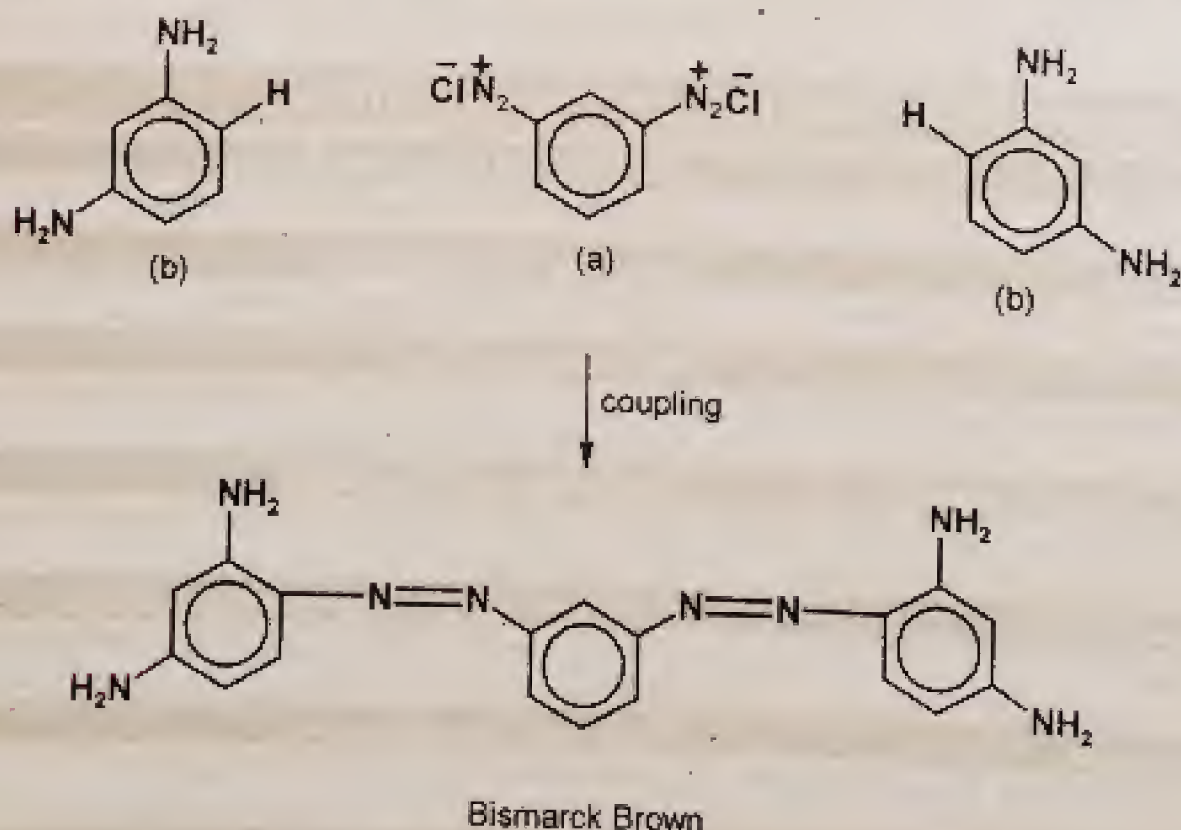
(ii) How is methyl orange prepared?

- Methyl orange is obtained from sulphanilic acid by the following steps:



(iii) How is Bismarck Brown prepared?

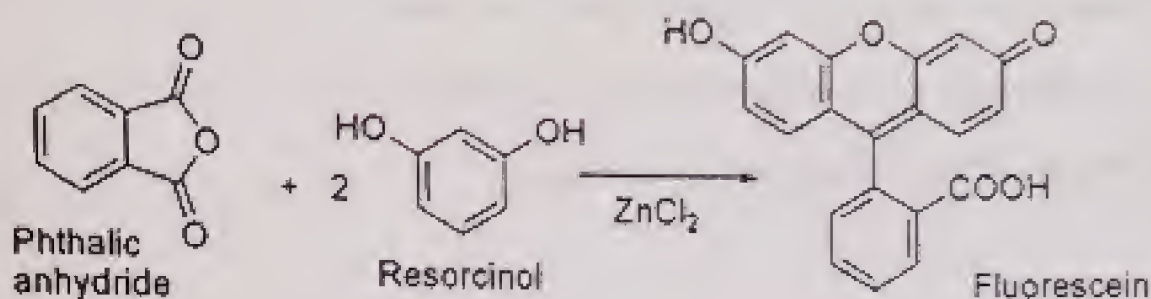
It is obtained by coupling tetrazotised m-diaminobenzene (a) with two molecules of m-diaminobenzene (b).





(iv) How is Fluorescein prepared?

It can be prepared from phthalic anhydride and resorcinol in the presence of zinc chloride via the Friedel-Crafts reaction.

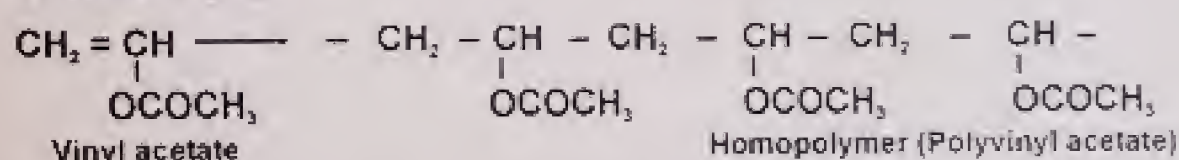


(v) Enlist different chemicals produced from ethylene.  
Page

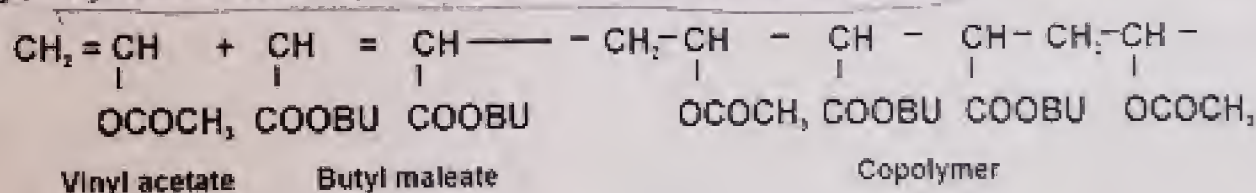
(vi) Write different chemicals produced from Toluene.  
Page

(vii) Differentiate between homopolymer and Copolymer

- Polymers which are synthesized from only one kind of monomer are called homopolymers.  
e.g.; Polyvinyl acetate



- Polymers which are prepared from more than one kind of monomer are called copolymers.  
e.g.; vinyl acetate and butyl maleate combine to give a copolymer



(viii) What is the difference between thermoplastic and thermosetting polymer.

- A thermoplastic polymer is one which softens on heating and becomes hard on cooling, e.g. Polyvinyl chloride (PVC)
- A thermosetting polymer is one which becomes hard on heating. It cannot be softened by heating, e.g., Bakelite.

(ix) How will you synthesize Nylon 6,6 from 1,3-Butadiene.  
Page 445

**Q3: Give detailed answers for the following questions.**

(i) What is chemical industry? Discuss different raw materials used in this industry.  
Page 427

(ii) What are dyes? How are they classified on the basis of structure?  
Page 430

(iii) What do you know about dyes? How are they classified on the basis of application?  
Page 434

(iv) Write a note on:

(a) Vat Dyes Page 434



(b) Mordant Dyes Page 435

(v) What is meant by Pesticides? Describe its types in detail.

Page 437

(vi) Describe the basic building block in petrochemicals technology.

Page 439

(vii) Describe raw materials and manufacturing process of Nail Polish.

Page 449

(viii) What are adhesives? Discuss its working and types.

Page 453



**TEST YOUR SKILLS**

Marks: 85

**OBJECTIVE**

Time: 20 Minutes

Marks: 17

Note: Over writing, cutting, erasing using ball pencil will result in loss of marks

(i) Light organic industries produce

(a) Dyes

(b) polymers

(c) petroleum fuels

(d) None

(ii) Raw materials are taken from

(a) atmosphere

(b) hydrosphere

(c) biosphere

(d) all

(iii) An example of Azo dye is

(a) Methyl orange

(b) m-diaminobenzene

(c) Naphthol yellow

(d) Mordant green

(iv) Which of the following is a dark - blue crystalline compound, insoluble in water & used for dyeing cotton by the vat process?

(a) Anthraquinone dye

(b) Indigo dye

(c) Triaminobenzene dye

(d) Azo dye

(v) In which of the following dye is central nitrogen bonded to four aromatic rings?

(a) Azo dyes

(b) Triarylmethene dyes

(c) Indigo dye

(d) Anthraquinone dyes

(vi) Ethylene is converted to ethanol via

(a) hydration

(b) condensation

(c) addition

(d) polymerization

(vii) Vinyl chloride is polymerized to produce

(a) Polyethylene

(b) polyvinyl chloride

(c) polyacetylene

(d) polybutene

(viii) Solvents produced from petrochemicals are

(a) Ethanol & acetone

(b) benzene & toluene

(c) isopropyl alcohol & xylene

(d) all

(ix) Which of the following is an example of condensation polymerization?

(a) polystyrene

(b) Polyvinyl chloride

(c) Nylon 6,6

(d) polyethylene

(x) Polymer which is prepared from more than one kind of monomer is called

(a) Homopolymer

(b) copolymer

(c) Addition polymer

(d) None

(xi) Petrochemicals are classified into how many classes?

(a) one

(b) two

(c) three

(d) four

(xii) Which of the following is not a raw material for nail polish?

(a) Pearl

(b) Castor oil

(c) Resorcinol

(d) Nitrocellulose

(xiii) In early days hair dyes were made from

(a) plants

(b) Animals

(c) metallic compounds

(d) both a & c

(xiv) A chemical compound which is meant to stick things together

(a) Nail polish

(b) Lipstick

(c) Hair dye

(d) Adhesive

(xv) In hair dyes resorcinol is used as

(a) Dye

(b) Anticorrosive

(c) modifier

(d) adjuvant

(xvi) In nail polishes solvent used is

(a) water

(b) butyl stearate

(c) benzene

(d) castor oil

(xvii) Which of the following solvent is used as nail polish remover?

(a) water

(b) acetone

(c) benzene

(d) castor oil

**(i) SUBJECTIVE**

(ii) Time: 2:35 Hours

Total Marks Section B and C: 68

(iii) Section - B (Marks 42) (14 × 3 = 42)

Q2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines.

- (1) (a) What are commodity chemicals? (02)
- (b) What are fine chemicals? (01)
- (2) (a) Name main sources for raw materials used in industries (01)
- (b) Which raw materials are obtained from atmosphere? (02)
- (3) (a) Differentiate between B / C & BOC (01)
- (b) Give examples of few natural products (02)
- (4) (a) What is meant by performance chemicals? (01)
- (b) Give share of different types of chemicals in global market? (1.5)
- (5) (a) What are requirements of process safety management? (1.5)
- (b) Differentiate between classical & industrial chemistry? (03)
- (6) What is a dye? Which properties it must have? On which basis they are classified? (03)
- (7) Differentiate between.
  - i) Pesticides & Insecticides
  - ii) Fungicides & herbicides.



- (8) (a) What are molluscicides? (01)  
 (b) Differentiate between selective & non-selective herbicides (02)  
 (9) (a) What do you mean by petrochemicals? (02)  
 (b) Name few chemicals produced from toluene. (01)  
 (10) What is industrial importance of ethylene? (03)  
 (11) (a) Differentiate between thermoplastics & thermosetting plastics. (02)  
 (b) Why Nylon 6,6 is called so? (01)  
 (12) What are uses of (03)  
 i) PVC ii) Nylon 6,6  
 (13) (a) How vinyl chloride is prepared from acetylene? (02)  
 (b) Write formula of adipic acid & hexamethylene diamine (01)  
 (14) (a) Define adhesives. (02)  
 (b) Give few examples of natural adhesives. (01)  
 (15) Give composition of nail polish (03)  
 (16) (a) What is composition of lipstick? (02)  
 (b) What type of wax is used as raw material of lipstick? (01)  
 (17) (a) How many steps are involved in manufacturing of lipstick? (02)  
 (b) Give percentage of alcohol & pigment in lipstick. (01)  
 (18) (a) How is Fluorescein prepared? (02)  
 (b) Give an example of a copolymer (01)  
 (19) (a) How will you prepare Nylon 6,6 from 1, 3 Butadiene? (02)  
 (b) Give uses of Nylon 6,6. (01)

**Section - C**

- Note:** Attempt any TWO questions. All questions carry equal marks. (2 × 13 = 26)
1. a) What are elements of the process safety management program? (05)  
 b) What are azo dyes? Give their examples. (04)  
 c) Write a note on Triaryl methane Dyes. (04)  
 2. a) How dyes are classified on the basis of methods of application? (04)  
 b) What are different types of pesticides? (05)  
 c) Differentiate between addition & condensation polymerization. (04)  
 3. a) Describe the basic building block in petrochemical technology. (04)  
 b) Write down steps manufacturing of lipstick involved in. (05)  
 c) What are different types of adhesives? (04)



## CHAPTER # 23

ENVIRONMENTAL  
CHEMISTRY**INTRODUCTION:**

It is the branch of chemistry which deals with the chemicals and other pollutants in the environment resulting directly and indirectly from human activities.

It is the study of the sources, chemical reactions, transportation of the chemicals and their adverse effects on human beings.

**Environment pollutant**

Any substance in the environment, which adversely affects the human health, quality of life and the natural functioning of ecosystem, is known as environmental pollutant.

**Primary Pollutants**

The pollutants which directly comes into the atmosphere from the source are called primary pollutants. e.g. oxides of nitrogen and volatile organic compounds (VOCs) created from fossil fuel combustion etc.

**Secondary Pollutants**

The pollutants which are derived from primary pollutants by chemical reactions in the atmosphere are called secondary pollutants.

e.g. sulphuric acid, nitrogen monoxide, carbonic acid, hydrofluoric acid, peroxyacetyl-nitrate (PAN)

**COMPONENTS OF THE ENVIRONMENT:**

- (1) **Atmosphere:** Gases surrounding the earth
- (2) **Hydrosphere:** Concerned with all water bodies i.e. ocean, rivers, streams lakes, glaciers and ground water reservoirs.
- (3) **Lithosphere:** Concerned with hard and rigid rocky earth crust.
- (4) **Biosphere:** Area on earth with support life i.e. air, lakes, etc.

**ATMOSPHERE:**

- Our surrounding on earth is called atmosphere.
- It consists of gases i.e.  $N_2$ , CO, He, Ne, Kr, Xe and water vapours.
- Its thickness is about 1000 km above the surface of earth.

The gases present in the atmosphere are very important in the following ways:

- (i) These gases absorb harmful radiations (cosmic rays and electromagnetic radiation) of Sun to protect life on earth. Otherwise these rays are very harmful to living things on earth.
  - (ii)  $N_2$  is used by nitrogen fixing bacteria
  - (iii)  $O_2$  is necessary for breathing in animals.
  - (iv)  $CO_2$  is necessary for photosynthesis in plants and
  - (v) Water vapours are responsible for sustaining life on earth.
- Atmosphere has been divided into four layers:
    1. Troposphere      2. Stratosphere      3. Mesosphere      4. Thermosphere
- First two layer are of more concern to human life. I.e. troposphere and stratosphere.

**CHEMISTRY OF TROPOSPHERE:**

- Troposphere is very close to earth in which we live.
- It extends up to 20km. it contains all those gases which are present in our atmosphere



It is important due to

- (1) Different pollutants (Their sources and effects and smog (development and chemistry))
- (2) Effects and chemical reactions occur during acid rain, green house effect and global warming
- (3) Role of automobile in air pollution

## SMOG

It is a combination of smoke and fog i.e. 'sm' from smoke and 'og' from fog

### Industrial Smog:

Under the right conditions, the smoke and sulfur dioxide produced from the burning of coal can combine with fog to create industrial smog.

### Photochemical smog

It is a condition that develops when primary pollutants (oxides of nitrogen and volatile organic compounds) created from fossil fuel combustion interact under the influence of sunlight to produce a mixture of hundreds of different and hazardous chemicals known as secondary pollutants.

### Major Chemical Pollutants in Photochemical Smog:

Toxic Chemical	Sources (Natural and Human)	Environmental Effects	Additional Notes
<b>Nitrogen Oxides (NO and NO<sub>2</sub>)</b>	<ul style="list-style-type: none"> <li>Combustion of oil, coal, gas in both automobiles and industry</li> <li>bacterial action in soil</li> <li>forest fires</li> <li>volcanic action</li> <li>lightning</li> </ul>	<ul style="list-style-type: none"> <li>Decreased visibility due to yellowish color of NO<sub>2</sub></li> <li>NO<sub>2</sub> contributes to heart and lung problems</li> <li>NO<sub>2</sub> can suppress plant growth.</li> <li>decreased resistance to infection</li> <li>may encourage the spread of cancer</li> </ul>	<ul style="list-style-type: none"> <li>All combustion products account for only 5 % of NO<sub>2</sub> in the atmosphere, most is from reactions involving NO</li> <li>concentrations likely to rise in the future</li> </ul>
<b>Volatile Organic Compounds (VOCs)</b>	<ul style="list-style-type: none"> <li>evaporation of solvents</li> <li>evaporation of fuels</li> <li>incomplete combustion of fossil fuels</li> <li>naturally occurring compounds like terpenes from trees</li> </ul>	<ul style="list-style-type: none"> <li>eye irritation</li> <li>respiratory irritation</li> <li>some are carcinogenic</li> <li>decreased visibility due to blue-brown haze</li> </ul>	<ul style="list-style-type: none"> <li>the effects of VOCs dependent on the type chemical</li> <li>samples show one or more different VOCs in atmosphere</li> <li>concentrations likely to continue to rise in future</li> </ul>
<b>Ozone (O<sub>3</sub>)</b>	<ul style="list-style-type: none"> <li>formed from photolysis of NO<sub>2</sub></li> <li>sometimes results from stratospheric ozone intrusions</li> </ul>	<ul style="list-style-type: none"> <li>bronchial constriction</li> <li>coughing, sneezing</li> <li>respiratory irritation</li> <li>eye irritation</li> <li>decreased crop yields</li> <li>retards plant growth</li> <li>damages plastics</li> <li>breaks down rubber</li> <li>harsh odor</li> </ul>	<ul style="list-style-type: none"> <li>concentrations of 0.1 ppm can reduce photosynthesis by 50 %</li> <li>people with asthma and other respiratory problems influenced the most</li> <li>can only be formed during daylight hours</li> </ul>
<b>Peroxyacetyl Nitrates (PAN)</b>	<ul style="list-style-type: none"> <li>formed by the reaction of NO<sub>2</sub> with VOCs (can be formed naturally in some environments)</li> </ul>	<ul style="list-style-type: none"> <li>eye irritation</li> <li>high toxicity to plants</li> <li>respiratory irritation</li> <li>damaging to proteins</li> </ul>	<ul style="list-style-type: none"> <li>was not detected or recognized in smog</li> <li>higher toxicity to plants than ozone</li> </ul>
<b>Carbon Oxide (CO and CO<sub>2</sub>)</b>	<ul style="list-style-type: none"> <li>Incomplete combustion of carbon containing fuels, (CO)</li> <li>Incomplete combustion of agricultural or slush matter, (CO)</li> <li>During the reaction in blast furnace (CO)</li> <li>Cigarette smoke (CO)</li> <li>Burning of fossil fuels produce CO<sub>2</sub></li> <li>Cultivation of Soil (CO<sub>2</sub>)</li> <li>Eruption of Volcanoes (CO<sub>2</sub>)</li> <li>Respiration of living organism, (CO<sub>2</sub>)</li> </ul>	<ul style="list-style-type: none"> <li>Causes Anoxia (Oxygen Starvation) result suffocation</li> <li>Causes Green house and Global Warming results climatic changes</li> <li>Causes Acid rain</li> <li>Causes Acid rain</li> <li>Respiratory irritation</li> </ul>	
<b>Oxides of Sulphur (SO, SO<sub>2</sub>)</b>	<ul style="list-style-type: none"> <li>Volcanic Eruption</li> <li>Burnt of oil &amp; coal</li> <li>Sulphide ores are roasted</li> </ul>	<ul style="list-style-type: none"> <li>Causes acid rain</li> <li>Respiratory irritation</li> <li>Loss of green color in plants</li> <li>Fading in color of Fabrics, leathers, paper and paints</li> </ul>	



## b) CHEMISTRY OF PHOTOCHEMICAL SMOG (CHEMICAL REACTIONS IN THE ATMOSPHERE)

- The development of photochemical smog is primarily determined by an abundance of nitrogen oxides and volatile organic compounds in the atmosphere and the presence of particular environmental conditions.
- The following conditions must occur to begin the chemical process of photochemical smog development.
  - ✓ **Sunlight.**
  - ✓ The production of **oxides of nitrogen (NO<sub>x</sub>)**.
  - ✓ The production of **volatile organic compounds (VOCs)**.
  - ✓ Temperatures greater than 18 degrees Celsius.
- If the above criteria are met, several reactions will occur producing the toxic chemical constituents of photochemical smog.
- The formation of two most dominant toxic components, **ozone (O<sub>3</sub>)** and **peroxyacetyl nitrate (PAN)** is given below. PAN is primarily created from volatile organic compounds.
- Nitrogen dioxide** can be formed by one of the following reactions. The **nitrogen oxide (NO)** acts to remove ozone (O<sub>3</sub>) from the atmosphere and this mechanism occurs naturally in an unpolluted atmosphere.
 
$$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$$

$$\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{other products}$$
- Sunlight can break down **nitrogen dioxide (NO<sub>2</sub>)** back into **nitrogen oxide (NO)**.
 
$$\text{NO}_2 + \text{sunlight} \rightarrow \text{NO} + \text{O}$$
- The **atomic oxygen (O)** formed in the above reaction then reacts with one of the abundant oxygen molecules (which makes up 20.94 % of the atmosphere) producing **ozone (O<sub>3</sub>)**.
 
$$\text{O} + \text{O}_2 \rightarrow \text{O}_3$$
- Nitrogen dioxide (NO<sub>2</sub>)** can also react with radicals produced from volatile organic compounds in a series of reactions to form toxic products such as **peroxyacetyl nitrates (PAN)**.
 
$$\text{NO}_2 + \text{R} \rightarrow \text{products such as PAN}$$

It should be noted that ozone can be produced naturally in an unpolluted atmosphere. However, it is consumed by nitrogen oxide. The introduction of volatile organic compounds results in an alternative pathway for the nitrogen oxide. Although still nitrogen dioxide is formed but ozone is not consumed. Therefore ozone concentrations can be elevated to toxic levels.

## QUICK QUIZ-1:

(i) **What is environmental chemistry?**

It is the branch of chemistry which deals with the chemicals and other pollutants in the environment resulting directly and indirectly from human activities.

It is the study of the sources, chemical reactions, transportation of the chemicals and their adverse effects on human beings.

(ii) **What is smog? What are its types?**

It is a combination of smoke and fog i.e. 'sm' from smoke and 'og' from fog"

It is of two types:

**Industrial Smog:**

Under the right conditions, the smoke and sulfur dioxide produced from the burning of coal can combine with fog to create industrial smog.



**Photochemical smog:**

It is a condition that develops when primary pollutants (oxides of nitrogen and volatile organic compounds created from fossil fuel combustion) interact under the influence of sunlight to produce a mixture of hundreds of different and hazardous chemicals known as secondary pollutants.

**(iii) What are different sources and environmental effects of:**

**(a) Ozone**

Sources: It is formed from photolysis of  $\text{NO}_2$ . Sometimes formed from stratospheric ozone intrusions

Environmental Effects: It causes following environmental effects

bronchial constriction, coughing, Sneezing, respiratory irritation, eye irritation, decreased crop yields, retards plant growth, damages plastics, breaks down rubber, harsh odor

**(b) Carbon oxides**

Sources:

The sources of carbon oxides are:

- Incomplete combustion of carbon containing fuels. (CO)
- Incomplete combustion of agricultural or slush matter, (CO)
- During the reaction in blast furnace (CO)
- Cigarette smoke (CO)
- Burning of fossil fuels produce  $\text{CO}_2$
- Cultivation of Soil ( $\text{CO}_2$ )
- Eruption of Volcanoes ( $\text{CO}_2$ )
- Respiration of living organism. ( $\text{CO}_2$ )

Environmental Effects:

The carbon oxides have following environmental effects

- Causes Anoxia (Oxygen Starvation) result suffocation
- Causes Green house and Global Warming results climatic changes
- Causes Acid rain
- Causes Acid rain
- Respiratory irritation

**(c) Sulphur oxides.**

Sources:

The sources of sulphur oxides are:

- Volcanic Eruption
- Burnt of oil & coal.
- Sulphide ores are roasted

Environmental Effects:

The sulphur oxides have following environmental effects

- Causes acid rain
- Respiratory irritation.
- Loss of green color in plants
- Fading in color of Fabrics, leathers, paper and paints.

**(iv) For the development of photochemical smog, what conditions are necessary?**

The following conditions must occur to begin the chemical process of photochemical smog development.

- **Sunlight.**
- The production of **oxides of nitrogen ( $\text{NO}_x$ ).**
- The production of **volatile organic compounds (VOCs).**
- Temperatures greater than 18 degrees Celsius.



**Exercise Q3 (ii):** Write a comprehensive note on acid rain.

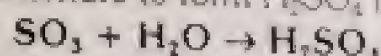
### ACID RAIN

The pH of unpolluted rain water is 5.6. The rain water having pH less than 5 is considered as acid rain.

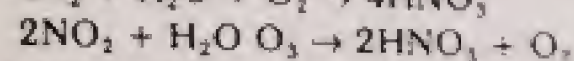
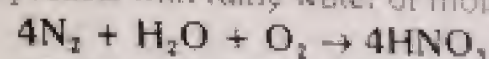
#### Explanation

We know that air contains  $\text{SO}_2$ ,  $\text{NO}_2$  and  $\text{CO}_2$ .

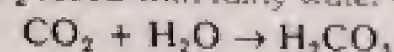
- (1)  $\text{SO}_2$  present in air undergoes photolytic and catalytic oxidation to form  $\text{SO}_3$  which reacts with rainy water or moisture to form  $\text{H}_2\text{SO}_4$  i.e.



- (2)  $\text{NO}_2$  reacts with rainy water or moisture in the presence of  $\text{O}_3$  and  $\text{O}_2$  and produces  $\text{HNO}_3$  i.e.



- (3)  $\text{CO}_2$  reacts with rainy water or moisture to form  $\text{H}_2\text{CO}_3$  i.e.



- (4) In some countries due to release of  $\text{HCl}$  by volcanic eruption, there is temporary acid rain.  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{CO}_3$  formed as above come down the atmosphere as acid rain or acid snow. As far as  $\text{H}_2\text{CO}_3$  is concerned, it has no severe effects on animals, plants or any other things.

**Quick Quiz-2 (ii):** Write down different effects of acid rain?

#### IMPACTS OR EFFECTS:

- (1) It makes the lakes so acidic that they can no longer support fish life.
- (2) The yield of agricultural crops is also reduced.
- (3)  $\text{HNO}_3$  acid rain gradually eats up lime stone and marble of the buildings and corrodes metals.
- (4) It fades the color of fabrics (e.g. cotton, nylon and rayon), leather and paper.
- (5) Causes extensive leaf-drop in plants.
- (6) It is very corrosive and attacks skin.
- (7) Acidification of soil and rocks can leach metals like Al, Hg, Pb and Ca and discharge them into water bodies. Then these heavy metals are eaten by fishes which proves very much dangerous for those animals and birds which eat these fishes.
- (8) It also damages steel, paint, plastic, cement, masonry work and sculptural materials.

### QUICK QUIZ-2

(i) What is acid rain?

The pH of unpolluted rain water is 5.6. The rain water having pH less than 5 is considered as acid rain.

(ii) Write down different effects of acid rain?

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(iii) List out those acid present in acid rain.

The acids are:  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{CO}_3$ . However,  $\text{H}_2\text{CO}_3$  has no severe effects.

(iv) Name those heavy metals which leach due to acidification of soil.

Acidification of soil and rocks can leach metals like Al, Hg, Pb and Ca and discharge them into water bodies.

### GREEN HOUSE EFFECT AND GLOBAL WARMING

The heating up of earth due to the trapping of infrared radiations (reflected from the earth's surface by  $\text{CO}_2$  layer in the atmosphere is called "green-house-effect".

#### Explanation

- There is a protective layer  $\text{O}_3$  gas in the atmosphere at a height between 15 km and 60 km.



- The thickest layer of  $O_3$  exists at a height of 23 km from the surface of the earth.
- A blanket of  $CO_2$  gas exists in lower part of the atmosphere (i.e. below 15 km).
- When sunlight, consisting of ultra-violet rays, visible light and infra-red rays falls on the top of the atmosphere, the harmful ultra-violet rays are absorbed by the  $O_3$  layer and hence do not reach the earth's surface.
- On the other hand, the visible light and infra-red rays pass through the  $CO_2$  layer and fall on the earth.
- Since the infra-red radiations have heating effect, they heat the earth and its various objects.
- The infra-red ray emitted by the extreme hot bodies like sun are of short wavelength.
- However, the earth and its various objects become hot, they start emitting infra-red rays (heat rays) of longer wavelength.
- The infra-red radiations of long wavelength emitted by the earth and its objects are absorbed by the  $CO_2$  layer in the atmosphere.
- Thus, the presence of  $CO_2$  in the atmosphere does not allow the infra-red radiation reflected by the earth's surface to go out of the atmosphere.
- In other words, we can say that the layer of  $CO_2$  gas in the atmosphere traps all the infra-red radiations coming from the earth's surface. These trapped infra-red rays heat the earth's atmosphere. Since the infrared rays coming from the earth cannot pass through the  $CO_2$  layer, the temperature of the earth is raised. This rise in the temperature is called Green House Effect.
- The rise in the temperature produced by the green-house-effect in the earth's atmosphere depends on the amount of  $CO_2$  gas present in the atmosphere.

#### **ORIGIN OF THE TERM "GREEN HOUSE EFFECT":**

- This effect is used in horticulture for the upbringing of green plants in a small house, whose walls and roof are made of glass-sheet. This is called green house.
- The glass walls and glass roof of the house allow the short wavelength infrared radiations, contained in sunlight, to go into green-house freely.
- However, these do not allow the long wavelength infrared radiations, reflected by the soil, plants and other contents of the green-house to go out.
- These trapped infrared radiations raise the temperature inside the green house.
- Thus, even without the internal supply of heat, the temperature inside the green house becomes higher than that outside it.

**Quick Quiz-2 (II):** What is the importance of green house effect?

#### **IMPORTANCE OF GREEN HOUSE EFFECT:**

- The green house effect is produced by the presence of  $CO_2$  layer in the atmosphere. It is very necessary for our existence on the earth.
- Due to green house effect,  $CO_2$  gas in the atmosphere does not allow the long wavelength infrared radiations reflected by the earth, to go out of the atmosphere. Hence the temperature of the earth's surface and its atmosphere is increased.
- The rise in temperature of the earth is very necessary for our existence on earth. It is because without it the whole earth would be converted into extremely cold planet. Thus, we shall not be able to have a normal life.

**Quick Quiz-2 (III):** Concentration of  $CO_2$  is responsible for climate changes. Comment.

#### **EFFECT OF EXCESS OF $CO_2$ PRESENT IN THE ATMOSPHERE:**

- If the atmosphere contains too much quantity of  $CO_2$ , the green house effect is considerably increased.
  - Thus, due to excess quantity of  $CO_2$  present in the atmosphere; the temperature of the earth is increased too much. This too much high temperature melts all the glaciers (snow-mountains) floods the low-lying areas of the earth.
  - It also changes the biological Activity of oceans and the patterns of cropping etc.
- Thus the presence of the excess of  $CO_2$  in the atmosphere brings about climate changes.



## QUICK QUIZ-2:

Is  $\text{CO}_2$  responsible for green house effect? If yes then how?

Yes,  $\text{CO}_2$  is responsible for green house effect. It is because when sun rays heat the earth, it emits infra-red radiations of longer wavelength. The layer of  $\text{CO}_2$  gas in the atmosphere traps all the infra-red radiations coming from the earth's surface. Thus, energy of rays is trapped by  $\text{CO}_2$ . Hence, the temperature of the earth is raised which is called Green House Effect.

What is the importance of green house effect?

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Concentration of  $\text{CO}_2$  is responsible for climate changes. Comment.

Page 497 Exercise Q 2 (ix)

## UTOMOBILE (POLLUTANTS AND CONVERTER)

- In automobiles during incomplete combustion of petrol, smoke of different gases comes out which pollute the atmosphere.
- The engine used in these motor vehicles are called internal combustion engines. It is because the petrol which is used as a fuel is burnt inside the engine and not separately.
- The exhaust gases contains  $\text{CO}$ ,  $\text{NO}$ ,  $\text{NO}_2$ , un-burnt carbon particles, some lead compounds, some alcohol and acids.
- All these substances are poisonous and hence pollute air.

## RODUCTION OF POLLUTANTS:

- Petrol is used as a fuel in automobile (car) engine. The main components of petrol are hydrocarbons. These hydrocarbons have general formula  $\text{C}_8\text{H}_{18}$  and hence are called octanes.
- Petrol burns very fast in a car engine. Due to short time available for burning, incomplete combustions of petrol takes place and some  $\text{CO}$ , unburnt carbon particles,  $\text{CO}_2$ , water vapors, some alcohol and acids are produced.
- $\text{CO}$  and carbon particles are emitted into the air and thus air is polluted.
- When petrol burns in a car engine, a very high temperature is produced.
- At this high temperature,  $\text{N}_2$  and  $\text{O}_2$  present in air of the engine combine together and form  $\text{NO}$  and  $\text{NO}_2$ . These gases also pollute the air.

Exercise Q3 (iii): How would you control air pollution? Describe different methods.

## ONTROL MEASURE:

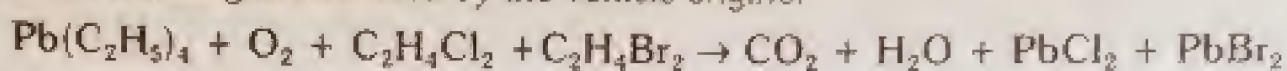
In order to control the air pollution caused by hydrocarbons and  $\text{CO}$  etc the following methods are used.

(i) By adding lead tetraethyl  $\text{Pb}(\text{C}_2\text{H}_5)_4$  to petrol:

- Suppose a vehicle uses petrol as fuel. Petrol burns very fast in the vehicle engine, e.g. the rate of combustion of petrol is very high and hence the time taken by the petrol for its combustion is very short. Due to this short time, the combustion of petrol is incomplete.
- $\text{Pb}(\text{C}_2\text{H}_5)_4$  is added to the petrol to slow down the rate of combustion of petrol.
- $\text{Pb}(\text{C}_2\text{H}_5)_4$  provides more time to the petrol for its combustion and hence enables it to burn more completely.
- Due to this the quantity of unburnt hydrocarbons and  $\text{CO}$  coming out of the engine, with exhaust gases is reduced and hence air pollution is also minimized.
- $\text{Pb}(\text{C}_2\text{H}_5)_4$  is oxidized to  $\text{PbO}$  which gets deposited on the spark plugs and valves.
- In order to prevent the deposition of  $\text{PbO}$ , suitable amount of  $\text{C}_2\text{H}_5\text{Cl}_2$  and  $\text{C}_2\text{H}_5\text{I}_2$  are also added to the petrol along with  $\text{Pb}(\text{C}_2\text{H}_5)_4$ .



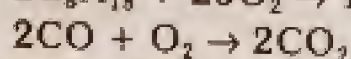
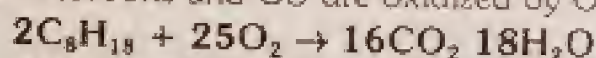
- These halides convert  $\text{PbO}$  into  $\text{PbCl}_2$  and  $\text{PbBr}_2$ . Both of these are volatile and hence come out with the exhaust gases emitted by the vehicle engine.



- Although the addition of  $\text{Pb}(\text{C}_2\text{H}_5)_4$  minimize the air pollution caused by unburnt hydrocarbons and the air gets polluted with dangerous  $\text{PbCl}_2$  and  $\text{PbBr}_2$ .

### (2) Catalytic oxidation/Converter:

- The pollution of air caused by the exhaust gases of the vehicle's engine can also be reduced by attaching a gas device with the vehicle's engine.
- In this device the exhaust gases can be mixed with more air and then burnt completely in the presence of platinum catalyst before they are discharged into the environment.
- Hydrocarbons and CO are oxidized by  $\text{O}_2$  of the air in presence of platinum catalyst.



The disadvantage of this method is that the platinum catalyst gets poisoned by  $\text{PbCl}_2$  and  $\text{PbBr}_2$  which are produced by the reaction between  $\text{Pb}(\text{C}_2\text{H}_5)_4$ ,  $\text{C}_2\text{H}_4\text{Cl}_2$  and  $\text{C}_2\text{H}_4\text{Br}_2$  in the presence of  $\text{CO}_2$ .

## QUICK QUIZ-3:

### (i) What is the role of tetraethyl lead in minimizing the air pollution?

Petrol burns too fast in the engine. Thus, tetraethyl lead,  $\text{Pb}(\text{C}_2\text{H}_5)_4$ , is added to the petrol to slow combustion. Thus, it gives more time to the petrol for its complete combustion. Hence, the quantity of unburnt hydrocarbons and CO coming out of the engine, with exhaust gases is reduced. Hence air pollution is also minimized.

### (ii) What is internal combustion engine

The engine used in these motor vehicles are called internal combustion engines. It is because the petrol which is used as a fuel is burnt inside the engine and not separately.

### (iii) Name those pollutants produced in automobile engines.

The exhaust gases from automobile engines contains CO, NO,  $\text{NO}_2$ , un-burnt carbon particles, some hydrocarbons, some alcohol and acids.

### (iv) What gas is produced due to high temperature of engine.

At this high temperature,  $\text{N}_2$  and  $\text{O}_2$  present in air of the engine combine together and form NO and  $\text{NO}_2$ .

### (v) What is drawback of lead tetraethyl used to control air pollution.

Tetraethyl lead,  $\text{Pb}(\text{C}_2\text{H}_5)_4$ , is oxidized to  $\text{PbO}$  which gets deposited on the spark plugs and valves.

In order to prevent the deposition of  $\text{PbO}$ , suitable amount of  $\text{C}_2\text{H}_4\text{Cl}_2$  and  $\text{C}_2\text{H}_4\text{Br}_2$  are also added to petrol along with  $\text{Pb}(\text{C}_2\text{H}_5)_4$ .

## CHEMISTRY OF THE STRATOSPHERE:

This layer of atmosphere is present 20-40 km above the earth and ozone is present in this layer at a height of about 28 kilometers.

The concentration of ozone in this layer is 10 ppm (10 parts per million)

In this layer of atmosphere, ozone is most important.

## PRODUCTION OF $\text{O}_3$ AND ITS TOXIC EFFECTS:

- $\text{O}_3$  is also produced in the upper part of the atmosphere by the action of sunlight on  $\text{O}_2$ .  

$$3\text{O}_2 \rightarrow 2\text{O}_3$$
- Some  $\text{O}_3$  is produced during various combustion processes taking place in the air.



- Traces of  $O_3$  in air do not harm but  $O_3$  of concentration more than 0.1 ppm is toxic and harmful to human beings.
- $O_3$  also attacks rubber products.

### **PROTECTIVE ACTION OF OZONE LAYER IN THE ATMOSPHERE:**

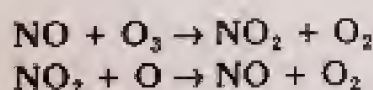
- The thickest layer of  $O_3$  exists at a height of 23 km from the surface of the earth.
- The  $O_3$  present in this layer absorbs harmful ultraviolet radiations coming from the sun.
- If these radiations reach the earth, they will cause skin cancer and will destroy the organic molecules necessary for life.
- Thus,  $O_3$  does not allow the ultra-violet radiations to reach the earth and thus saved from the harmful effects caused by these radiations.
- If  $O_3$  layer in the atmosphere disappears completely, then all the harmful ultra-violet radiations coming from the sun would reach the earth. It would cause skin cancer in men and animals and will also damage the plants.
- Hence, All the life on earth would then gradually be destroyed.

### **SOURCES OF DESTRUCTION/DESTROYING THE OZONE LAYER PRESENT IN STRATOSPHERE:**

- In 1980 scientists showed that there is a hole in the  $O_3$  layer.
- This hole was detected over the region of Antarctica.
- Due to the absence of  $O_3$  layer, the ultraviolet rays coming from the sun can pass through the hole and thus can reach the earth's surface.
- The ozone hole is due to the fact that the amount of  $O_3$  present in stratosphere is getting reduced day by day. Thus, the ozone layer is becoming thinner and thinner.
- The depletion of the ozone layer is due to the following sources.

#### **(1) Oxides of Nitrogen:**

- The oxides of nitrogen present in the atmosphere decompose  $O_3$  into  $O_2$  and are themselves regenerated.



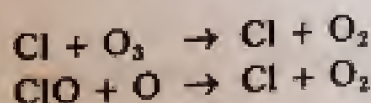
- Thus, the presence of nitrogen oxides in the atmosphere destroys the ozone layer.
- These oxides destroy about 70% of  $O_3$  found in the stratosphere.
- Greater is the amount of the oxides in the atmosphere greater is the percentage of  $O_3$  which is destroyed.

#### **(2) Nuclear Tests:**

Nuclear tests being conducted in the world generate high temperature. At high temperature, atmospheric nitrogen is favorably oxidized to NO. NO thus formed destroys ozone layer, as shown above.

#### **(3) Use of Chloro-Flouro Carbons:**

Fluoro-chloro-carbons are the fluoro-chloro methanes like, Freon-1 ( $CFCl_3$ ) and Freon-2 ( $CF_2Cl_2$ ). These are stable compounds. These are chemically inert and hence do not react with the substances. These are used as aerosol spray propellants, refrigerants, firefighting reagent and solvents for cleaning electronic components. When they enter stratosphere, they absorb ultraviolet solar radiations and get broken down into free atomic chlorine. This atomic chlorine decomposes  $O_3$  into  $O_2$  like NO gas.





### PROTECTION OF THE OZONE LAYER:

- Scientists are worried over the gradual destruction of ozone layer by the oxides of nitrogen and fluorine carbons.
- In order to save the destruction of  $O_3$  layer by fluoro-chloro carbons, their use should be banned. OR
- Some new types of substances should be discovered which may be used as aerosol spray propellants and should not react with  $O_3$  layer.

### SOME ALTERNATIVES TO CHLORO-FLUORO CARBONS (CFCs):

- The first CFC substitutes to be introduced were HCFCs such as  $CF_3CHCl_2$  and  $CHF_2Cl$  compounds. These have fewer chlorine atoms than other CFCs.
- HCFCs break down more readily in the atmosphere than CFCs and thus are less likely to reach the stratosphere.
- However, because they can cause some  $O_3$  destruction, they are scheduled to be phased out by 2030.
- Much better substitutes for CFCs are hydrofluorocarbons. These contain no chlorine.
- One of them  $CF_3CH_2F$  has been used successfully as a refrigerant and since 1994 has replaced Freon in nearly all car air conditioners.
- In electronic industries, soapy water followed by rinsing and air drying is now used instead of CFCs to clean micro circuits.
- Unfortunately, a serious problem is associated with the long term use of HFC. Like CFC and HCFCs they contribute to climate change.
- However researches are going on to find chemicals that are both effective refrigerant and environmental friendly.

### QUICK QUIZ-4:

- (i) *Ozone acts both useful as well as harmful. Justify the statement.*

The  $O_3$  absorbs the harmful ultra-violet radiations coming from the sun. Thus, it saves the life from the harmful effects of ultra-violet rays.

However, its high concentration in atmosphere is very harmful. It causes respiratory problems, attacks rubber, retards plant growth etc.

- (ii) *Enlist the possible alternatives to the use of CFCs.*

The possible alternatives to the use of chlorofluorocarbons (CFCs) are:

Hydrochlorofluorocarbons (HCFCs): e.g.  $CF_3CHCl_2$  and  $CHF_2Cl$ .

Hydrofluorocarbons (HFCs): e.g.  $CF_3CH_2F$

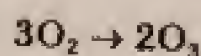
- (iii) *How  $O_3$  is decomposed by oxides of nitrogen*

The oxides of nitrogen present in the atmosphere decompose  $O_3$  into  $O_2$  and are themselves regenerated.



- (iv) *How ozone is produced*

$O_3$  is produced in the upper part of the atmosphere by the action of sunlight on  $O_2$ .



Some  $O_3$  is produced during various combustion processes taking place in the air.



## WATER POLLUTION AND WATER TREATMENT

The contamination of water with the substances which have adverse effects on human beings, animal and plants is called water pollution

The substances whose presence in the water makes it polluted are called pollutants.

### TYPES OF WATER POLLUTANTS

These are of following types:

#### SUSPENDED SOLID AND SEDIMENTS:

These are wastes which are not completely soluble but suspended in the water. These wastes include:

- (1) Oil spillage
- (2) Live-stock waste
- (3) Industrial wastes and
- (4) Leather tanneries

**Quick Quiz-5 (I):** Briefly describe about oil spillage as a source of water pollution and its effects on environment.

#### (I) OIL SPILLAGE:

- Petroleum is a complex mixture of many compounds which are mainly hydrocarbons.
- It is transported from one place to another through sea.
- The petroleum products are used as:
  - (i) Fuel
  - (ii) Lubricants manufacture of petrochemicals
  - (iii) Plastics
  - (iv) Electrical appliances
  - (v) Synthetic rubber
  - (vi) Detergents
- In order to prepare such a large varieties of substances, petroleum is handled on large scale in the world. So the oil spillage can take place and it creates serious problems.

#### Pollution of Water by Petroleum:

Water gets polluted by:

- (i) accidental oil spills
- (ii) leakage from cargo oil tankers in sea
- (iii) tanker trucks
- (iv) pipelines leakage during offshore exploration
- (v) leakage of under ground storage tanks

#### Oil Spillage and Animal Life:

- Many petroleum products are poisonous and create serious health problems to:
  - (i) Humans
  - (ii) Animals
  - (iii) Aquatic life
- Polycyclic hydrocarbons are carcinogenic even at very low concentration.
- Marine animals are seriously affected by soluble aromatic fractions of oil.
- The spilled oil damages the feather of the birds or fur of animals and sometimes causes their death.

#### Petroleum and Under Water Plants:

- When oil is spilled on the surface of sea then the light transmission is affected. Thus, the process of photosynthesis of plants does not remain much efficient.
- Moreover, the concentration of oxygen in water is decreased.



### (2) LIVE STOCK WASTE:

- Livestock waste is dumped on open land
- Sometimes it is discharged into sewage, canals or rivers
- This practice pollutes the surface and ground water. In this way serious problems are created for population
- Bacteria are present in the livestock waste. It contaminates the surface and ground water. This causes diseases like:
  - (i) Dysentery
  - (ii) Typhoid
  - (iii) Hepatitis

### (3) INDUSTRIAL WASTES:

#### Sources:

- Industries which are producing large quantities of industrial effluents are leather, tanneries, fertilizers, refineries, petrochemicals, textiles, foods, sugar, paper, pulp, paper board, rubber products etc.
- The waste products may also be waste heat, smoke solid or water effluent.

#### Pollutants:

- The industrial pollutants are highly toxic organic compounds and heavy metals like Pb, Cd, Cr, Hg, Sb etc.
- Oil greases, Mineral acids are also released in small quantities.
- These pollutants result in contamination of water and make it unsuitable for irrigation and drinking purposes.

#### Effects of Industrial pollutants:

- Heavy metal particles are highly toxic and do not have any safe limits
- When they are continuously ingested through food or water they get accumulated in the organisms and cause serious health problems like anemia, kidney diseases, nervous disorder, high blood pressure etc.

### (4) LEATHER TANNERIES:

- There are many leather tanning units working in Pakistan. Their sizes vary from cottage scale to industrial units.
- Leather industries use chromium salts which have +6 oxidation state of chromium.
- Only a few industries have the facility of waste treatment. This can be done by reducing  $\text{Cr}^{+6}$  oxidation states to  $\text{Cr}^{+3}$  oxidation state.  $\text{Cr}^{+3}$  is precipitated as  $\text{Cr}(\text{OH})_3$ .
- $\text{Cr}^{+6}$  salts are highly toxic and cause cancer.

### DISSOLVED SOLIDS

These are wastes which are dissolved/soluble in water completely. These wastes include:

- (1) Detergents
- (2) Pesticides
- (3) Chemical fertilizers

#### (1) DETERGENTS:

- Detergents are used in homes and industries for washing.
- After washing these detergents are thrown into water reservoirs.
- The amount of detergents in reservoirs is increasing day by day.
- This waste water containing detergents goes into rivers and finally reaches the ocean, which is harmful for life in seas.
- The detergents remove bound heavy metal ions like Pb, Cd and Hg and transport it from sediments in water. These metal particles are very toxic.



## 23) PESTICIDES:

- The pesticides are both toxic and persistent.
- Analysis of polluted water has shown that it contains pesticides which are toxic to fish.
- **Endrin** is reported to be toxic for catfish and other varieties of fish even if present in traces.
- **D.D.T.** affects the central nervous system of fish and toxaphene has been reported to cause bone degeneration in fish.

## 24) CHEMICAL FERTILIZERS:

- Nitrate/phosphate salts are generally used as fertilizers, to increase the yield of the crops.
- When these fertilizers are used in excess, some of their unused quantity is washed away from the agriculture lands into the ponds, lakes and river with rain water and thus pollute the water. Thus water is polluted, since it contains unused nitrate/phosphate salts.
- Similarly the waste water coming from the fertilizer industries also contains nitrogenous/phosphatic fertilizers. When these are washed away into the lakes and river with rain water, make the water polluted.
- The presence of nitrogenous/phosphatic fertilizers in water is harmful to the aquatic life and human beings in the following ways:
  - (i) The presence of the fertilizers in the polluted water increases the growth of algae and other aquatic plants. These later on undergo decomposition and produce disagreeable odor. These plants also deplete the amount of  $O_2$  dissolved in water and hence the survival of aquatic life becomes difficult or impossible.
  - (ii) After a long period, the lakes and slow moving waters which contains plant nutrients are converted into swamps (A swamp is an area of very wet land with wild plants growing in it) and marshes (A marsh is an area of land which is very wet and muddy).
  - (iii) The water containing nitrate salt is not fit for drinking by human beings. Moreover, this polluted water cannot be purified for drinking purposes.

**Exercise Q3 (iv):** What is Thermal Pollution? Discuss its sources and environmental effects.

## THERMAL POLLUTION

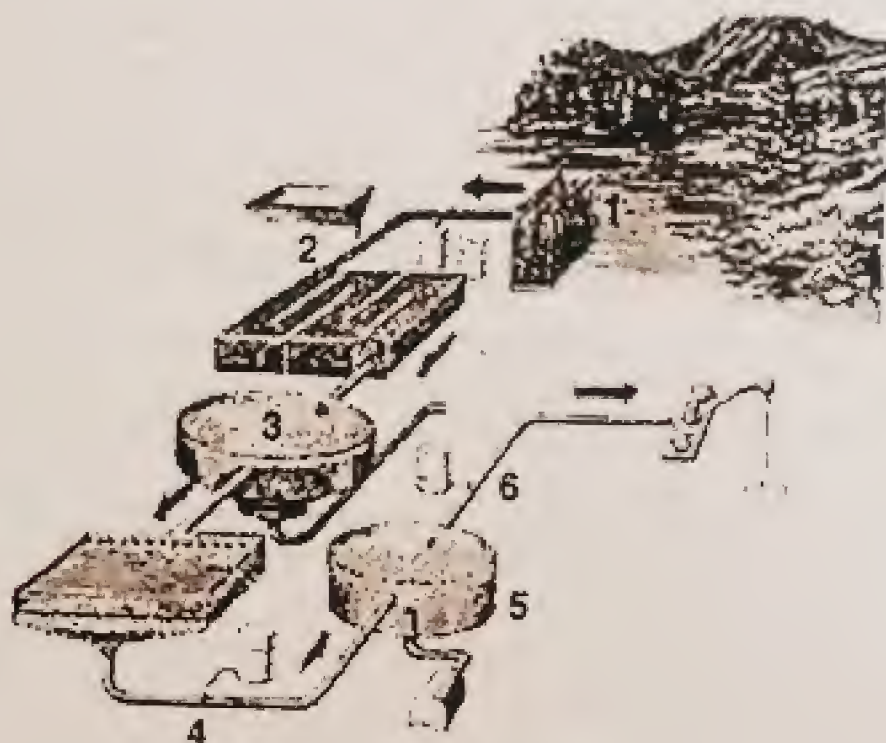
- Thermal pollution takes place because many electric generating companies use water in the process of cooling their generator. This heated water is then released into the system from which it was drawn, causing a warming trend of the surface, water.
- Thermal pollution results when the heated effluent is released into poorly flushed system. In these cases permanent temperature increase often result, which tend to decrease the solubility of dissolved oxygen. In lakes it also becomes possible to bring about nutrient redistributions and prolong summer stagnation periods.
- When heated water gets released into large, well-flushed marine systems there is little if any permanent temperature rise.
- There are however problems related to the operation of plants utilizing marine water in the cooling process.
- Evidence reveals that sea water tends to corrode the cooling pipes, which are generally constructed of a copper nickel alloy termed Monel. These metals readily dissolved in the heated seawater and are then released into the marine environment together with the heated effluent. This adds to the nickel and copper concentrations of these systems.
- In addition the screens covering the water intake pipes rapidly foul with marine organism, which decrease the flow of water into the plant. The screens have been commonly cleaned by using a concentrated detergent solution or copper sulfate. These cleaning materials have been then released into the contaminated the surrounding waters.



**Exercise Q3 (v):** What is waste water treatment? Discuss different methods of it.

### WASTE WATER TREATMENT: ANALYSIS/PURIFICATION OF WATER

- Industrial wastewater treatment covers the mechanisms and processes used to treat contaminated water before its release into the environment or its re-use.
- Most industries produce some wet waste. Although recent trends in the developed world are to minimize such production or recycle such waste within the production process.
- However, many industries remain dependent on processes that produce water based waste stream.



Water Treatment Plant

#### Do You Know?

About 97% of the water on earth is found in the oceans. Most of the rest is frozen in the polar ice caps and in glaciers.

### TREATMENT OF INDUSTRIAL WASTE WATER

The different types of contamination of wastewater require a variety of strategies to remove the contamination.

#### (A) SOLIDS REMOVAL

Most solids can be removed using simple sedimentation techniques with the solids recovered as slurry or sludge.

#### (B) OILS AND GREASES

- Many oils can be recovered from open water surfaces by skimming devices.
- However, hydraulic oils and the majority of oils that have degraded to any extent will also have a soluble or emulsified component. These require further treatment to eliminate.

#### (C) SOFT ORGANICS

- Organic material of plant or animal origin is usually possible to treat using extended conventional wastewater treatment processes.
- Problems can arise if the wastewater is excessively diluted with washing water or is highly concentrated such as neat blood or milk.
- The presence of cleaning agents, disinfectants, pesticides, or antibiotics can have detrimental impacts on treatment processes.



**(D) HARD ORGANICS**

- Synthetic organic materials including solvents, paints, pharmaceuticals, pesticides, coking products etc can be very difficult to treat.
- Treatment methods are often specific to the material being treated. Methods include distillation, adsorption, nitrification, incineration, chemical immobilization or landfill disposal.

**(E) ACIDS AND ALKALIS**

- Acids and alkalis can usually be neutralized under controlled conditions.
- Neutralization frequently produces a precipitate that will require treatment as a solid residue that may also be toxic.
- In some cases, gasses may be evolved requiring treatment for the gas stream.

**(F) TOXIC MATERIALS**

- Toxic materials including many organic materials, metals (such as zinc, silver, cadmium, thallium etc.) acids, alkalis, non-metallic elements (such as arsenic or selenium) are generally resistant to biological processes unless very dilute.
- Metals can often be precipitated out by changing the pH or by treatment with other chemicals.
- Many, however, are resistant to treatment or mitigation and may require concentration followed by land filling or recycling.

## QUICK QUIZ-5:

(i) Briefly describe about oil spillage as a source of water pollution and its effects on environment.  
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(ii) Enlist the diseases caused by live-stock.

Bacteria are present in the livestock waste. These cause different diseases like:

(a) Dysentery, (b) Typhoid, (c) Hepatitis

(iii) How industrial wastes pollute water?

The industrial pollutants are highly toxic organic compounds and heavy metals like Pb, Cd, Cr, Hg, As, Sb etc. Oil greases, Mineral acids are also release in small quantities.

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When Nitrate/phosphate fertilizers are used in excess, some of their quantity is washed away into the ponds, lakes and river with rain water and thus pollute the water.

The waste water coming from the fertilizer industries also contains nitrogenous/phosphatic fertilizers. When these are washed away into the lakes and river with rain water, they make the water polluted.

(v) How solubility of oxygen in water is reduced by thermal pollution

Thermal pollution occurs when the heated effluent is released into poorly flushed system. In these cases permanent temperature increase may occur, which decreases the solubility of dissolved oxygen.

(vi) What is swamp?

A swamp is an area of very wet land with wild plants growing in it. It is generally a low-lying area where water collects.



## Various Parameters of Water Analysis

Following table will help us to determine the water quality.

**Table** Water-quality Indicators

Parameter	Significance	Level
Dissolved oxygen	General indicator of water quality ; source of $O_2$ for respiration	Minimum acceptable level, 4-5 mg/liter ; 10-15 mg/liter for reproduction of desirable fish
Total suspended solids	Clog fish gills, bury eggs, reduce light penetration, increase heat absorption	Dependent on location
Total dissolved solids	Represents total mineral content which may or may not be toxic	A maximum of 400 mg/liter for diverse fish populations
BOD	Amount of dissolved oxygen removed during decomposition of organic matter in a given time ; a general indicator of contamination due to biodegradable organics	<i>BOD Water Status</i> 1 mg/liter Very clean 2 mg/liter Clean 3 mg/liter Fairly clean 5 mg/liter Doubtful 10 mg/liter Contaminated
COD	Indicates the concentration of materials oxidizable by chemical reaction	0.5 mg/liter indicates very clean streams
pH	Indicates the addition of acids or bases	pH depends on actual system
Iron	Excessive amounts can clog fish gills ; indicates drainage from iron-bearing sediments, mines, industrial processes	A maximum of 0.7 mg/liter for diverse fish populations
Manganese	Concentration low in natural systems due to low solubility ; high concentrations indicates contamination	A maximum of 1 mg/liter is a common criterion for stream quality



Table (Contd.)

Parameter	Significance	Level
Copper	Indicates drainage from copper-bearing sediment, mines, plating, or other industrial sources	A maximum of 0.02-10 mg/liter is a common criterion for stream quality
Zinc	Indicates mine drainage or industrial input	A maximum of 1 mg/liter is a common criterion for stream quality
Hg, Cd, Pb, Ni, Cr, Ag, etc.	Indicates industrial input	A maximum of 1 mg/liter is a common criterion for stream quality
Nitrate	A major plant nutrient; in high-concentrations it can promote excessive plant growth; major sources are fertilizers, sludge, and sewage	A maximum of 0.3 mg/liter to prevent excessive fertilization of streams
Phosphate	A major plant nutrient; major sources are detergents, fertilizer, sewage	A maximum of 0.03-0.40 mg/liter total inorganic phosphate is a common criterion

## QUICK QUIZ-6

### (i) What is green chemistry

The design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances is called green chemistry.

Green chemistry emphasizes the design and creation of chemicals that are not hazardous to people or the environment.

### (ii) Give importance of green chemistry

Green chemistry emphasizes the design and creation of chemicals that are not hazardous to people or the environment. Thus, it is effective in reducing the impact of chemicals on human health and the environment.

### (iii) What is spinosad

Spinosad is an insecticide manufactured by fermenting a naturally occurring soil organism. It was registered by the EPA as a reduced-risk insecticide in 1997. It has following advantages.

- It does not leach, bioaccumulate, volatilize, or persist in the environment.
- In fields, it left 70 to 90 percent of beneficial insects unharmed.
- It has a relatively low toxicity to mammals and birds. It is slightly to moderately toxic to aquatic organisms. However, it is toxic to bees.



(iv) Give principle of green chemistry

The design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances is called green chemistry.

Green chemistry emphasizes the design and creation of chemicals that are not hazardous to people and environment.

(v) What is synthetic efficiency

An efficient chemical process ensures that the maximum amount of starting materials is used up to give a product so that no atom is wasted. This is called Synthetic Efficiency or Atom Economy.

(vi) Give use of renewable Feed stocks

Renewable feedstocks are those from other processes or products derived from agricultural area. They can be used in different preparations whenever technically or economically feasible.

Exercise Q3 (vi) Write a note on Green Chemistry

## GREEN CHEMISTRY

The term green chemistry, introduced in 1991, is defined as

The design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances is called green chemistry.

- Green chemistry emphasizes the design and creation of chemicals that are not hazardous to people or environment.
- It has been applied to a wide range of industrial and consumer goods, including paints, dyes, herbicides, pesticides, plastics, medicines, electronics, dry cleaning, energy generation, and water purification.

## WHY GREEN CHEMISTRY?

- Green chemistry is effective in reducing the impact of chemicals on human health and the environment.
- In addition, many companies have found that it can be cheaper and even profitable to meet environmental goals. Profits derive from higher efficiency, less waste, better product quality, and reduced liability.
- Many environmental laws and regulations target hazardous chemicals, and following all these requirements can be complicated.
- But green chemistry allows companies to comply with the law in much simpler and cheaper ways.
- Finally, green chemistry is a fundamental science-based approach. Addressing the problem of hazard at the molecular level, it can be applied to all kinds of environmental issues.
- Since 1991, there have been many advances in green chemistry, in both academic research and industrial implementation.
- For example, **Spinosad**, an insecticide manufactured by fermenting a naturally occurring soil organism, was registered by the EPA as a reduced-risk insecticide in 1997.
- Spinosad does not leach, bioaccumulate, volatilize, or persist in the environment and in field tests left 70 to 90 percent of beneficial insects unharmed. It has a relatively low toxicity to mammals and birds and is slightly to moderately toxic to aquatic organisms, but is toxic to bees until it dries.



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## THE TWELVE (12) PRINCIPLES OF GREEN CHEMISTRY

The aim of green chemistry is to reduce chemical related impact on human health and virtually eliminate contamination of the environment through dedicated, sustainable prevention programs.

Green chemistry searches for alternative, environmentally friendly reaction media and at the same time strives to increase reaction rates and lower reaction temperatures.

Sigma-Aldrich is dedicated to providing alternative products designed with the health and safety of its employees, customers, and the public in mind.

The green chemistry concept applies innovative scientific solutions to solve environmental issues posed in the laboratory.

**Paul T. Anastas**, an organic chemist working in the Office of Pollution Prevention and Toxins at the EPA, and **John C. Warner** developed the Twelve Principles of Green Chemistry in 1991.

The twelve Principles focus on reducing the volumes of chemicals used and pollution prevention.

These principles can be grouped into "Reducing Risk" and "Minimizing the Environmental Footprint."

### (i) REDUCING RISK IN THE LABORATORY

This group includes four principles

- (1) **Use Safer Chemicals** – Utilize performance chemicals that have the lowest levels of toxicity.
- (2) **Design Less Hazardous Synthesis Methods** – Where feasible, make use of synthetic or biosynthetic methods that pose little or no toxicity to human health and the environment.
- (3) **Use Safer Solvents and Reaction Conditions** – Search for the most up-to-date information on green solvents that will optimize your process and provide a safer working environment.
- (4) **Accident Prevention** – Select substances that minimize the potential for explosions, fires and chemical releases into the environment.

### (ii) MINIMIZING THE ENVIRONMENTAL FOOTPRINT

This group includes eight principles

- (1) **Waste Minimization and Prevention** – Develop chemical synthesis techniques, which reduce or prevent waste. It is better to prevent waste than to clean it up after its creation.
- (2) **Use of Catalysts Instead of Stoichiometric Quantities** – Catalytic reactions inherently use smaller quantities of chemicals to carry out a specified transformation.
- (3) **Reduce the Use of Chemical Derivatives** – The use of protecting groups or other forms of temporary modification of a functionality adds to the total waste incurred in a synthetic route.
- (4) **Synthetic Efficiency (Atom Economy)** – An efficient chemical process ensures that the maximum amount of starting materials is used in the final product so that no atom is wasted.
- (5) **Taking Advantage of Chemicals Designed for Degradation** – Reduce the effect on the environment by using chemicals that are designed to be biodegradable.
- (6) **Establishment of In Process Controls for Pollution Prevention** – To avoid the formation of hazardous substances, adopt real-time analysis and in process monitoring during synthesis.
- (7) **Use of Renewable Feedstocks** – Use raw materials or renewable feedstocks (waste from other processes or products derived from agricultural streams) whenever technically or economically feasible.
- (8) **Encourage Energy Efficiency** – The realization of the economical and environmental impact of energy use in a chemical process and the development of alternative means to reduce the impact.



## SOCIETY, TECHNOLOGY AND SCIENCE

### RADIATION POLLUTION

Radioactive substances and nuclear radiations produced during nuclear reaction affect our environment adversely and thus radioactive pollution created.

#### Sources of radioactive pollution and its effects

- (i) **Radioactive Cloud:** Low level radioactive liquid wastes, radioactive gaseous wastes, and dusts are released during nuclear explosions. The radioactive gaseous wastes are injected into the upper layer of atmosphere where, due to cooling they condense to fine dust particles and thus radioactive cloud is formed. This cloud moves in the direction of the wind, settles down slowly to the surface of the earth and thus pollutes water and soil.
- (ii) **Energy:** The radioactive substances produce energy which is so strong that the living cells are damaged or destroyed.
- (iii) **Tumors:** People working with radioactive elements develop tumors.
- (iv) **Radioactive Elements:** Radioactive element like strontium 90 affects our soil. Through this human beings and animals are also affected adversely.
- (v) **Nuclear Explosions:** Nuclear explosions which are operated in sea make sea water polluted. This affects the aquatic life.
- (vi) **Gamma radiations:**
  - Among the radioactive radiations, gamma radiations are the most dangerous, since they have high energy and big penetrating power.
  - These radiations can, therefore, pass freely in the human body, where they lose energy. Thus, they destroy the living cells by converting them into charged particles (ions). These charged particles are chemically very reactive and hence disturb cell membrane. Hence, it reduces the effectiveness of enzymes and even damage genes and chromosomes.
  - All this results in diseases like leukaemia and cancer.
- (vii) **Nuclear Radiations:** In a nuclear reactor, U-235 is used as a nuclear fuel. It undergoes nuclear fission and energy is produced. Nuclear radiations are produced in the processes like mining and enrichment of U-235 taking place in the nuclear reactor. These radiations can leak from the reactor and therefore, damage the health of the human beings and animals.

#### Control measures for minimizing radioactive pollution

##### Disposal of Nuclear Waste

The waste material produced in the mining, enrichment and fission of U-235 inside the reactor are collectively called nuclear wastes.

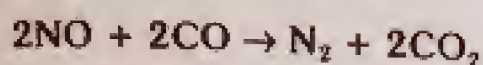
At present most of the nuclear wastes are being sorted in strong leak proof containers. These will be disposed off whenever a safe method of their disposal is found out.

##### Using catalytic Converters

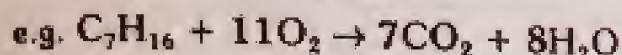
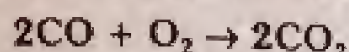
A catalytic converter removes pollutant gases from the exhaust by oxidizing or reducing them.

- The exhaust gases pass through a converter containing a precious metal catalyst, usually an alloy of platinum and rhodium.
- Several reactions may take place.
- $\text{NO}_x$  and CO may take part in a redox reaction which neatly removes both of them at the same time:
- $\text{NO}_x$  oxidizes CO to  $\text{CO}_2$  and is reduced to harmless nitrogen gas.

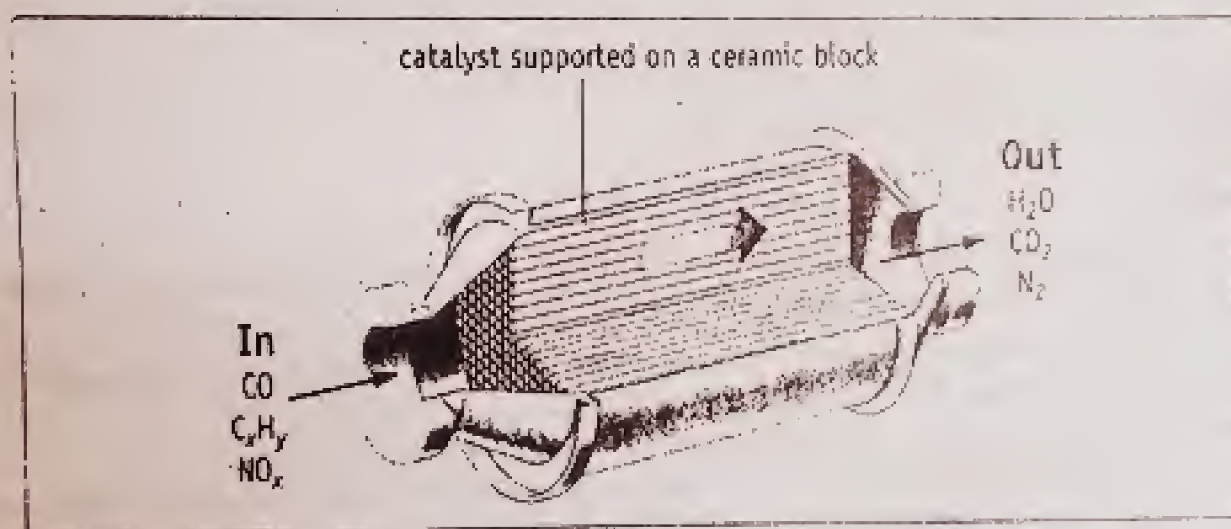




- CO and  $\text{C}_x\text{H}_x$  are oxidized by air;



- For all three of these reactions happen, it is necessary to use a three way converter and to have an oxygen monitor fitted to the engine.
- This checks the quantity of oxygen going into the engine to make sure there is enough to carry out the oxidation reactions.
- The overall result of passing exhaust gases through this kind of catalyst system is to convert CO,  $\text{NO}_x$  and  $\text{C}_x\text{H}_y$  to relatively harmless  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .
- The catalytic reactions do not start working until the catalyst has reached a temperature of about  $200^\circ\text{C}$  so they are not effective until the engine has warmed up.
- Catalyst systems of this type cost several hundred pounds. It is mainly due to the high cost of the precious metal they contain. The catalyst is poisoned by lead, so unleaded fuel must always be used.



## WATER POLLUTION

*The waste water from household and industries without treatment to river is dangerous*

### Sources:

- It comes from places like factories, farms and industry.
- Waste water from manufacturing or chemical processes in industries contributes to water pollution.
- Industrial waste water usually contains specific and readily identifiable chemical compounds. However, in many cases the pollution in our rivers comes from our homes.
- Incorrect plumbing could mean that waste water from dishwashers, washing machines, sinks, baths and even toilets.
- Other impurities include organic materials and plant nutrients that tend to rot.
- The main organic materials are food and vegetable waste, plant nutrient come from chemical soaps, washing powders, etc.
- These flushed directly into a local river. These 'misconnected' pipes are a common cause of pollution in rivers and streams, especially in towns and cities.
- Today, many people dump their garbage into streams, lakes, rivers, and seas. Thus making water bodies becomes the final resting place of cans, bottles, plastics, and other household products.
- The various substances used for keeping our houses clean add to water pollution as they contain harmful chemicals.



### Types of Drainage Systems

There are normally two forms of drainage - surface water and foul water.

#### i) Surface water drains, or 'storm drains'

These carry rainwater from road surfaces and rooftops into local rivers and streams and flows into the sea untreated.

#### ii) Foul water drains

These carry waste water from toilets, sinks, baths and household appliances to the sewage treatment works. This water is treated before it can safely flow back into river and streams...

### Pollution in America

- Americans generate 1.6 million tons of household hazardous waste per year.
- The average home can accumulate as much as 100 pounds of household hazardous waste in the basement or garage and in storage closets. When improperly disposed of, household hazardous waste can create a risk to people and the environment.
- Paints, cleaners, oils, batteries, and pesticides are examples of just a few of the common household hazardous wastes that need special disposal.

### Eutrophication

When fresh water is artificially supplemented with nutrients, it results in an abnormal increase in the growth of water plants. This is known as eutrophication.

- The discharge of waste from industries, agriculture, and urban communities into water bodies generally stretches the biological capacities of aquatic systems.
- Chemical run-off from fields also adds nutrients to water.
- Excess nutrients cause the water body to become choked with organic substances and organisms.
- When organic matter exceeds the capacity of the micro-organisms in water that break down and recycle the organic matter, it encourages rapid growth of algae.
- When the algae die, their remains add to the organic wastes already in the water; eventually, the water becomes deficient in oxygen.
- Anaerobic organisms (those that do not require oxygen to live) then attack the organic wastes, releasing gases such as methane and hydrogen sulphide. These are harmful to the oxygen-requiring (aerobic) forms of life. The result is a foul-smelling, waste-filled body of water.
- Untreated sewage effluent in the water causes oxygen levels to drop drastically. The sewage fungus covers the bed of the watercourse like a blanket. In more severe cases the river can no longer support fish, insects and animals that live in and around the water.

### Effects of Polluted Water

- Polluted water is unsuitable for drinking, recreation, agriculture, and industry.
- It diminishes the aesthetic quality of lakes and rivers.
- More seriously, contaminated water destroys aquatic life and reduces its reproductive ability.
- Eventually, it is a hazard to human health. Nobody can escape the effects of water pollution.
- Once an aquifer is contaminated, it may be unusable for decades. The residence time can be anywhere from two weeks or 10 000 years.



**AIR POLLUTION****The Biggest Source of Air Pollution:**

- The biggest source of air pollution is automobiles.
- In past there was bull cart, donkey carts animals were used by.
- Now-a-days Aeroplane, cars, buses and trains are used for transportations. These vehicles need energy for their working in the form of petrol or gas to provide energy for motion of vehicle.
- The end product of this burning includes energy plus different gases include hydrocarbons, Nitrogen oxides, carbon monoxide, Benzene, sulphur, heavy metals and particles. These gases enter into air and pollute it. When human breaths in such polluted environment it causes asthma, coughing, nausea, chest pain, bronchitis, diseases etc.

**Effects of Air Pollution**

- It is estimated that usually 24000 deaths occur due to air pollution because pollution damages the central Nervous System.
- Automobiles are responsible for depletion of ozone in the stratosphere sheet because of source of CFCs entering the atmosphere which is escape from vehicle air condition (ACs)
- Vehicles are responsible
  - ✓ for 80% pollution in metropolitan region,
  - ✓ three fold increases in energy consumption for global warming. It is because burning of fuel produces  $\text{CO}_2$ .

**Control of Air Pollution****(i) Ways to improve the impact of cars.**

Ways to improve impacts of car like uses of small cars, cleaner cars, efficient engine catalytic converters are compulsory and use of biofuel. The following measures may be helpful

- Use of Fuel cells:** It causes only water comes out as its exhaust. Electrical vehicle poses problem because of range of batteries and sleep.
- Use of Hybrid electric petrol:** It cuts down the fuel wastage and effects the high energy fuel on board e.g. in Delhi they demolished the buses run on diesel
- Restricts the occurs to the cities or part of cities**  
e.g. Chester, York, Oxford have given free space for parking at the edge of town.
- Improve information about road condition and public transport**  
e.g. Zurich zone referendum given the priority to trams, trolleys, buses, parking prohibitions 50% of all the trips as by means of public transport
- Polluter pay**  
It is another solution where the pollution emitted by the car is measured and the driver is charged on the basis of level multiplies the distance travel.

**(ii) Technological improvements**

Several technological innovations have been made from 1970 onwards to make more friendly technology. Technological improvements include.

- Technological changes to reduce cooling zone of engine wall and reduce hydrocarbon and carbon monoxide emission.
- Computer control at IC engine.
- Catalytic converter technology (CCT) emission
- Trap oxidizers and ceramic filter in Diesel vehicles
- Direct injection fuel efficient Diesel



## OZONE

### Occurance

- Ozone layer is found in the stratosphere approximately 10-50 km above the earth surface.
- Ozone molecules have three atoms of oxygen instead of the normal two.

### Advantage

- The ozone layer protects us from the harmful effects of certain wave lengths of ultra violet (UV) coming from the sun., specially UVB.
- Any significant decrease in ozone in the atmosphere would result in an increase of UVB radiation reaching the earth surface.
- Increase in levels of UVB radiation can result in the increase in skin cancer; suppress the immune system; eye disorder including cataract and effect plants, animals and plastic materials.

### Ozone depletion

- In 1985, scientists discovered that there is severe ozone depletion in the Antarctic region, which was confirmed by American Satellite observations.
- Chlorofluorocarbons (CFCs) were invented in 1928 found many used in foams, refrigeration and air conditioners, solvent, fire extinguishers etc. these CFCs are long lived and their emissions reach the stratosphere and cause ozone depletion. This has been dramatically confirmed through Antarctic ozone hole.
- The United Nations Environment Programme (UNEP) has been addressing the issue of depletion of the ozone layer since 1977 and in 1981 UNEP's Governing Council set up a working group to prepare a global framework convention for protection of ozone layer.
- By reducing the use of CFCs we can protect ozone layer for saving the environment from harmful effects.
- Montreal protocol on substances that deplete the ozone layer was finally agreed upon on 16<sup>th</sup> September 1987 and adopted by the Government in this protocol ozone depleting substances are banned.

### Alternatives to ozone-depleting halocarbons

- Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) are alternative halocarbons.
- These are being used to replace ODS in industrial and commercial applications and their use is becoming more widespread.
- Other alternatives to ODS include ammonia, carbon dioxide and hydrocarbons.

### The relationship between ozone-depleting substances and their halocarbon alternatives and global warming

- Ozone-depleting substances (ODS) and their halocarbon alternatives have a direct global warming potential and contribute to climate change.
- The production of some ozone depleting substances (e.g. CFCs) has been ceased worldwide resulting in emission reductions of ozone-depleting substances into the atmosphere.
- However, emissions of other ODS (e.g. hydrochlorofluorocarbons [HCFCs]) and ODS alternatives (e.g. hydrofluorocarbons [HFCs]) is expected to continue to increase.
- HFCs are ODS refrigerants alternatives and their use is becoming more widespread.
- Although HFCs have no ozone-depletion potential they do have high global-warming potential and are thousands of times more potent greenhouse gases than carbon dioxide.
- Regulations that prevent or minimize ODS and other halocarbons emissions serve a dual environmental benefit of lowering emissions that destroy the ozone layer and contribute to climate change.



**Are ozone-depleting substances still an important environmental concern?**

Although the production and use of many ODS has been phased out. However, the control of ODS emissions continues to be an important environmental issue. It is because the destruction of the earth's protective stratospheric ozone layer causes increased health risks and environmental impacts, such as cataracts, skin cancer and climate change.

**NATURAL WATER PURIFICATION METHODS**

There are several, natural ways that you can purify water.

- *In the event of an emergency it may become necessary to purify the water for drinking in order to avoid getting sick.*
- *Though many people think purifying water is difficult. However, there are a number of simple, natural means of purifying water that can easily be used in an emergency.*

**SAND**

- One of the most common ways that water is purified is by passing it through sand and soil.
- If contaminated water (say urine) is poured onto fine sand, the water is going to travel down until it reaches the saturation level.
- The other chemicals that are mixed with the water, though, will be held back by the sand until only the water is left.

This method of water purification is used in many sewage treatment facilities as a big part of separating water out of the waste that goes through the plant.

**BOILING**

- Water can be boiled to make it more pure.
- Boiling water kills bacteria and other germs in the water, which makes it safer to drink.
- **Procedure**
  - ✓ Water is poured into a sealed pot, with a tube leading out of it.
  - ✓ The water turns into steam, and the steam escapes through the tube.
  - ✓ The tube transports the steam to another container, where the steam condenses back into water.
  - ✓ This process can eliminate more contaminants from water (such as salt), but it is also more complicated.

**CLOTH FILTRATION**

- Cloth filters can be used to help keep larger contaminants out of water.
- **Procedure:**
  - ✓ This process is very simple.
  - ✓ Pour the water through a cloth, or through several layers of cloth.
  - ✓ The cloths' weave will strain the water and hold back impurities.
  - ✓ This is the same process that happens when a coffee filter is used, except that the filter is paper rather than cloth.
  - ✓ Paper can work as well.
  - ✓ The coffee filters or similar devices may be used instead of a clean cloth to strain your water.



## How rain water seepage through hazardous waste dumpsites can dissolve in drinking water supplies

### Hazardous waste:

Hazardous waste is waste that is dangerous or potentially harmful to our health or the environment.

- Hazardous wastes can be liquids, solids, gases, or sludges.
- They can be discarded commercial products, like cleaning fluids or pesticides, or the by-products of manufacturing processes.
- It is very important to dispose off hazardous waste carefully otherwise it contaminate the air, water, and soil.

### Groundwater:

Groundwater is rain water or water from surface water bodies, like lakes or streams, that soaks into the soil and bedrock. It is stored underground in the tiny spaces between rocks and particles of soil.

Groundwater contaminants come from two categories of sources:

#### Point sources

These are Landfills, leaking gasoline storage tanks, leaking septic tanks, and accidental spills.

#### Non-point sources

Infiltration from farm land treated with pesticides and fertilizers is an example of a non-point source.

- Among the more significant point sources are municipal landfills and industrial waste disposal sites. When either of these occur in or near sand and gravel aquifers, the potential for widespread contamination is the greatest.
- Leaks of petroleum products have been increasing over the last two decades. It is because underground steel tanks installed in large numbers in the 1950s and 1960s have become corroded. Before 1980, most underground tanks were made of steel. Without adequate corrosion protection, up to half of them leak by the time they are 15 years old.
- Groundwater dissolves many different compounds. Most of these substances have the potential to contaminate large quantities of water. e.g., one litre of gasoline can contaminate 1 000 000 litres of groundwater. This problem is particularly severe in the Atlantic provinces where there is a high usage of gasoline. In many cases, the problem is noticed long after the aquifer is contaminated, e.g., when consumers start tasting or smelling gasoline.
- Groundwater can become contaminated in many ways. Chemicals from hazardous wastes buried in unsecured landfills. If rain water or surface water comes into contact with contaminated soil while seeping into the ground, it can become polluted and can carry the pollution from the soil to the groundwater. The contaminants can also spread to wells or surface water, making it unsafe to drink.
- Groundwater can also become contaminated when liquid hazardous substances themselves soak down through the soil or rock into the groundwater. Some liquid hazardous substances do not mix with the groundwater but remain pooled within the soil or bedrock. These pooled substances can act as long-term sources of groundwater contamination as the groundwater flows through the soil or rock and comes into contact with them.
- Groundwater contamination is extremely difficult, and sometimes impossible, to clean up.
- Apart from chemical pollutants the major culprits are Bacteria and Viruses which cause most of the commonly found water borne diseases.

Bacterial diseases: Gastro-enteritis, Typhoid, Cholera, Paratyphoid, Dysentery and Diarrhea.

Viral diseases: Polio, Dysentery, Gastro-enteritis, Diarrhea and Jaundice (Hepatitis)



**REPLACING CFCs**

- Few compounds have CFCs combination of non-flammability, non-toxicity and inertness. For uses such as refrigeration and aerosols it is necessary to find compounds with exactly the right boiling point.
- **Hydrofluorocarbon (HFCs):**  
Some of the important replacements for these uses are the hydrofluorocarbons, CFCs (also known as hydrofluorocarbon or HFCs.). An example is 1,1,1,2-tetrafluoroethane,  $\text{CH}_3\text{CH}_2\text{F}$ , which is used as a refrigerant.
- **HFCs are comparatively safe:**
  - ✓ HFCs have the advantage that they contain no Cl atoms, so they do not release damaging Cl radicals in the stratosphere.
  - ✓ Moreover, their molecules include C-H bonds, which are relatively reactive. It means that these compounds break down in the atmosphere more quickly than CFCs so they do not persist for so long.



## KEY POINTS

- Actually our atmosphere has been divided into four layers
- 1- Troposphere 2- Stratosphere 3- Mesosphere 4- Thermosphere
- Photochemical smog is formed only when the atmosphere contains soot particles, hydrocarbons and oxides of nitrogen (mainly  $\text{NO}_x$ )
- $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{CO}_3$  formed in air come down the atmosphere as acid rain or acid snow
- In automobiles during incomplete combustion of petrol, we get smoke of different gases which pollute our atmosphere. The engines used in these motor vehicles are called internal combustion engines.
- When petrol burns in a car engine, a very high temperature is produced. At this high temperature  $\text{N}_2$  and  $\text{O}_2$  present in air of the engine combine together and form  $\text{NO}$  and  $\text{NO}_2$ . These gases pollute the air.
- Nuclear tests being conducted in the world generate high temperature. At high temperature, atmospheric nitrogen is favorably oxidized to  $\text{NO}$ .  $\text{NO}$  thus formed destroys ozone layer.
- By keeping the vehicle properly tuned for the optimum ignition of fuels. This method also prevents air pollution caused by  $\text{CO}$  and hydrocarbons present in the exhaust fumes of the vehicles.
- Use of fluoro-chloro carbons (e.g. Freon-1 and Freon-12) as aerosol spray propellant destroys the  $\text{O}_3$  layer, as oxides of nitrogen do.
- Water gets polluted by: accidental oil spills, leakage from cargo oil tankers in sea, tanker trucks, pipelines leakage during offshore exploration, leakage of under ground storage tanks.
- Polycyclic hydrocarbons are carcinogenic even at very low concentration. Marine animals are seriously affected by soluble aromatic fractions of oil. The spilled oil damages the feather of the birds or fur of animals and sometimes causes their death.
- Surfactants are organic compounds having polar or hydrophilic groups such as  $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$ ,  $\text{NH}_4^+$  or non-polar or lyophilic groups soluble in water.
- The waste heat from electrical generating stations is transferred to cooling water obtained from local water bodies such as a river, lake, or ocean.
- Water purification is a process of removing harmful substances and odor from a raw water source.



# EXERCISE

**Q1: Select the right answer from the choices given with each question.**

- (i) Air is polluted by:  
(a) Toxic materials (b) Hydrocarbons (c) Harmful gases (d) All of above
- (ii) Which of following gas is not pollution?  
(a)  $\text{SO}_2$  (b)  $\text{CO}$  (c)  $\text{CO}_2$  (d)  $\text{NO}_2$
- (iii) Oxides of sulfur and nitrogen react with oxygen to form:  
(a) Bases (b) Acids (c) Salts (d) All of above
- (iv) Oxidizing smog consists of high concentration of:  
(a)  $\text{SO}_2$  (b) Ozone (c)  $\text{NO}_2$  (d)  $\text{Cl}_2$
- (v) Thickness of ozone is:  
(a) 20-25 km (b) 25-28km (c) 30-32km (d) 20-30km
- (vi) Ozone is destroyed by:  
(a)  $\text{SO}_2$  (b)  $\text{NO}_2$  (c) Chlorofluorocarbons (d) None of above
- (vii) In leather industry:  
(a) Chromium (VI) is used (b) Chromium (III) is used (c) Nickel is used (d) Aluminum is used
- (viii) Water is purified:  
(a) Aeration (b) Coagulation (c) Disinfection (d) All of above
- (ix) The Ecosystem is the smaller unit of:  
(a) Biosphere (b) Lithosphere (c) Atmosphere (d) Hydrosphere
- (x) When chlorine is passed through water then the disinfection is done due to the production?  
(a)  $\text{HCl}$  (b)  $\text{HOCl}$  (c)  $\text{NOCl}$  (d)  $\text{HClO}_4$
- (xi) Peroxyacetyl nitrate (PAN) is an irritant to human beings and it affects  
(a) eyes (b) ears (c) stomach (d) nose
- (xii) Fungicides are the pesticides which  
(a) control the growth of fungus (b) kill insects (c) kill plants (d) kill herbs

## ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (d) All of above Air is polluted by toxic materials like PAN, hydrocarbons and gases like $\text{SO}_2$ etc.	(ii) Ans: (c) $\text{CO}_2$ $\text{CO}_2$ is generally not considered as pollution as it is needed by plants for photosynthesis.
(iii) Ans: (b) Acids This is the cause of acid rain	(iv) Ans: (b) Ozone Ozone is present in oxidizing smog. It is an oxidizing agent
(v) Ans: (b) 25-28km The thickness of ozone in stratosphere is 25-28 km	(vi) Ans: (c) Chlorofluorocarbons Chlorofluorocarbons play a major role in the destruction of ozone layer.
(vii) Ans: (a) Chromium (VI) is used Chromium (VI) is used in leather industry	(viii) Ans: (d) All of above (a), (b) and (c) are stages of water purification
(ix) Ans: (a) Biosphere In ecosystem both living and non-living environment is present, so it is a biosphere.	(x) Ans: (b) $\text{HOCl}$ $\text{HOCl}$ decomposes to release atomic oxygen ( $[\text{O}]$ ) which oxidizes the cell wall of bacteria.
(xi) Ans: (a) eyes PAN causes irritation in eyes	(xii) Ans: (a) control the growth of fungus Fungicide controls the growth of fungus

**Q2: Give brief answers for the following questions.**

- (i) What are components of environment?  
(a) Atmosphere (b) Hydrosphere  
(c) Lithosphere (d) Biosphere
- (ii) Briefly discuss the role of atmosphere in our environment?  
Our surrounding on earth is called atmosphere are very important because:



(a) These gases absorb harmful radiations (cosmic rays and electromagnetic radiation) of Sun to protect life on earth. Otherwise these rays are very harmful to living things on earth.

(b)  $N_2$  is used by nitrogen fixing bacteria

(c)  $O_2$  is necessary for breathing in animals.

(d)  $CO_2$  is necessary for photosynthesis in plants and

(e) Water vapours are responsible for sustaining life on earth.

(iii) Enlist different layers of our atmosphere.

Atmosphere has been divided into four layers:

1. Troposphere      2. Stratosphere      3. Mesosphere      4. Thermosphere.

(iv) What are sources of air pollution?

Sources of air pollution are:

(a) Nitrogen oxides ( $NO$  and  $NO_2$ )

(b) Oxides of sulphur ( $SO_2$  and  $SO_3$ )

(c) Volatile organic compounds (VOCs)

(d) Carbon monoxide ( $CO$ )

(v) What are the important air pollutants?

Important air pollutants are:

(a) Nitrogen oxides

(b) Sulphur oxides

(c) Peroxyacetyl nitrates

(d) Peroxybenzyl

(e) Volatile organic compounds

(f) Carbon monoxide

(vi) What are the sources of  $CO$  emission? Discuss its effects.

**Source of  $CO$**

- Incomplete combustion of carbon containing fuels ( $CO$ )
- Incomplete combustion of agricultural or slush matter, ( $CO$ )
- During the reaction in blast furnace ( $CO$ )
- Cigarette smoke ( $CO$ )

**Effects**

- Causes Anoxia (Oxygen Starvation) result suffocation
- Causes Green house and Global Warming results climatic changes
- Causes Acid rain
- Causes Acid rain
- Respiratory irritation

(i)

(vii) Differentiate between (i) Industrial and photochemical smog (ii) Primary and secondary pollutants.

**a. Industrial smog**

Under the right conditions, the smoke and sulfur dioxide produced from the burning of coal can combine with fog to create industrial smog

**b. Photochemical smog**

It is a condition that develops when primary pollutants (oxides of nitrogen and volatile organic compounds created from fossil fuel combustion) interact under the influence of sunlight to produce a mixture of hundreds of different and hazardous chemicals known as secondary pollutants

**Primary Pollutants**

The pollutants which directly comes into the atmosphere from the source are called primary pollutants.

e.g. oxides of nitrogen and volatile organic compounds (VOCs) created from fossil fuel combustion etc.



**Secondary Pollutants**

The pollutants which are derived from primary pollutants by chemical reactions in the atmosphere are called secondary pollutants.

e.g. sulphuric acid, nitrogen monoxide, carbonic acid, hydrofluoric acid, peroxyacetyl-nitrate (PAN)

(ell) How does photochemical smog differ from reducing smog?

Photochemical smog is a condition that develops when primary pollutants (oxides of nitrogen and volatile organic compounds created from fossil fuel combustion) interact under the influence of sunlight to produce a mixture of hundreds of different and hazardous chemicals known as secondary pollutants. While reducing smog is formed when smoke and sulphur dioxide produced from burning of coal combine with fog.

(lx) What is global warming?

When sunlight consists of ultraviolet rays, visible light and infrared rays falls on the top of the atmosphere the harmful ultra violets rays are absorbed by  $O_3$  layer and hence do not reach on the other hands, the visible light and infrared rays pass through the  $CO_2$  layer and falls on the earth. Since the infrared radiations have heating effect they heat the earth and its objects. This is called global warming.

(x) What are the latest predictions about global warming?

- If the atmosphere contains too much quantity of  $CO_2$ , the green house effect is considerably increased.
- Thus, due to excess quantity of  $CO_2$  present in the atmosphere; the temperature of the earth is increased too much. This too much high temperature melts all the glaciers (snow-mountains) floods the low-lying areas of the earth.
- It also changes the biological Activity of oceans and the patterns of cropping etc

(xi) What gases are responsible for green house effects?

The gases are

- (a)  $CO_2$  and CO      (b) Methane      (c) CFCs      (d) Nitrogen oxides

(xii) Briefly discuss effects of acid rain.

- It makes the lakes so acidic that they can no longer support fish life.
- The yield of agricultural crops is also reduced.
- $HNO_3$  acid rain gradually eats up lime stone and marble of the buildings and corrodes metals.
- It fades the color of fabrics (e.g. cotton, nylon and rayon), leather and paper
- Causes extensive leaf-drop in plants.
- It is very corrosive and attacks skin.
- Acidification of soil and rocks can leach metals like Al, Hg, Pb and Ca and discharge them into water bodies. It also damages steel, paint, plastic, cement, masonry work and sculptural materials.

(xiii) What are sources and environmental effects of? (a) VOCs (b) PAN

Page 462 given in Table

(xiv) What are effects of excess of  $CO_2$  present in atmosphere?

- If the atmosphere contains too much quantity of  $CO_2$ , the green house effect is considerably increased.
- Thus, due to excess quantity of  $CO_2$  present in the atmosphere; the temperature of the earth is increased too much. This too much high temperature melts all the glaciers (snow-mountains) floods the low-lying areas of the earth.
- It also changes the biological Activity of oceans and the patterns of cropping etc.

(xv) Discuss the sources and typical effects of  $SO_2$  as pollutant.

Page 462 given in Table

(xvi) Briefly discuss the sources and typical effects of oxides of nitrogen.

Page 462 given in Table

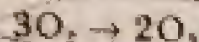


(xviii) What is ozone? How does it work as safeguard?

The ozone ( $O_3$ ) is the protective layer in the atmosphere, present at in stratosphere between 15-25 km. The thickest layer of  $O_3$  exists at a height of 23 km from the surface of the earth. The  $O_3$  layer shields the harmful ultra-violet radiations coming from the sun. Thus, it saves the life from the harmful ultra-violet rays.

(xviii) How ozone is formed in stratosphere?

$O_3$  is produced in the upper part of the atmosphere by the action of sunlight on  $O_2$ .



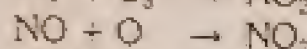
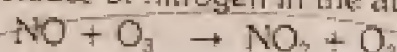
Some  $O_3$  is produced during various combustion processes taking place in the air.

(xix) What do you know about "Ozone hole"?

In 1985, scientists discovered that there is severe ozone depletion in Antarctic region. Chlorofluorocarbons reach stratosphere and cause ozone depletion. This has been dramatically visible through Antarctic ozone hole.

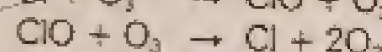
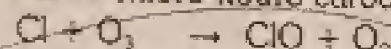
(xx) How is ozone layer depleting?

(i) oxides of nitrogen in the atmosphere converts  $O_3$  into  $O_2$



Nuclear tests generate high temperature. Due to this the nitrogen is oxidized to NO which destroys ozone layer.

(ii) Use of chloro-fluoro carbons destroy ozone layer by decomposing  $O_3$  into  $O_2$ .



(xxi) What are the effects of ozone layer depletion?

If  $O_3$  layer in the atmosphere disappears completely, then all the harmful ultra-violet radiations coming from the sun would reach the earth. It would cause skin cancer in men and animals and will also damage the plants. Hence, All the life on earth would then gradually be destroyed.

(xxii) What should we do to save ozone?

In order to save the destruction of  $O_3$  layer by fluoro-chloro carbons, their use should be banned. Some new types of substances should be discovered which may be used as aerosol spray propellants and should not react with  $O_3$  layer.

Leaded petrol should be used in automobiles

(xxiii) What is water pollution? Write different types of water pollution?

The contamination of water with the substances which have adverse effects on human beings, animals and plants is called water pollution.

Sources of water pollution are

- Oil spillage
- Live-stock waste
- Industrial waste
- Leather tanneries

(xxiv) Briefly discuss the effects of water pollution.

- Polluted water is unsuitable for drinking, recreation, agriculture, and industry.
- It diminishes the aesthetic quality of lakes and rivers.
- The contaminated water destroys aquatic life and reduces its reproductive ability.
- The polluted water causes several diseases



(i) **How preliminary treatment of waste water is done?**

In Preliminary treatment most of the suspended particles are removed which are visible.

(ii) **What is primary treatment of waste water?**

Primary treatment involves the removal of sand particles and other particles which are visible.

(iii) **What is secondary treatment of waste water?**

Secondary treatment involves:

- Solids removal
- Oils and greases
- Soft organics
- Hard organics
- Acid and alkalis
- Toxic materials

(iv) **How would avoid from thermal pollution?**

The companies use hot water in cooling their generators. When hot water is released in water bodies, it decreases the solubility of dissolved oxygen. Thus causes serious threat to life in water. So, the companies should decrease the temperature of hot water before discharging into water bodies.

**Q3: Give detailed answers for the following questions.**

(i) **Describe different chemical reaction occurring in our atmosphere.**

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(ii) **Write a comprehensive note on acid rain.**

Page 465

(iii) **How would you control air pollution? Describe different methods.**

Page 467

(iv) **What is Thermal Pollution? Discuss its sources and environmental effects.**

Page 473

(v) **What is waste water treatment? Discuss different methods of it.**

Page 474

(vi) **Write a note on Green Chemistry.**

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**TEST YOUR SKILLS**

**Marks: 85**

**OBJECTIVE**

Time: 20 Minutes

Marks: 17

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks

Q1. Circle the correct option i.e. A/B/C/D) Each part carries one mark.

- (i)  $N_2$  in atmosphere is used
  - (a) by plants for photosynthesis
  - (b) by nitrogen fixing bacteria
  - (c) for breathing in animals
  - (d) All
- (ii) An example of primary pollutant is:
  - (a) Oxides of nitrogen
  - (b) volatile organic compounds
  - (c)  $H_2SO_4$
  - (d) both a & b
- (iii) Ozone in atmosphere causes:
  - (a) Bronchial constriction
  - (b) eye irritation
  - (c) damage of proteins
  - (d) acid rain
- (iv) Which of the following pollutant causes acid rain?
  - (a)  $SO_2$
  - (b)  $NO_2$
  - (c)  $CO_2$
  - (d) All
- (v) Which heavy metals are leached due to acidification of soil?
  - (a) Al, Fe, Hg, Ca
  - (b) Al, Hg, Pb, Ca
  - (c) Al, Fe, Ag, Hg
  - (d) Hg, Pb, Fe, Ca
- (vi) The thickest layer  $O_3$  gas exist at a height of ..... from surface of the earth?
  - (a) 23 km
  - (b) 2.3 km
  - (c) 23m
  - (d) 230m
- (vii) Which of following gas is not pollution?
  - (a)  $SO_2$
  - (b) CO
  - (c)  $CO_2$
  - (d)  $NO_2$
- (viii) Oxidizing smog consist of high concentration of:
  - (a)  $SO_2$
  - (b) ozone
  - (c)  $NO_2$
  - (d)  $Cl_2$
- (ix) Leather industries use Cr salts which have ..... oxidation state of Cr.
  - (a) +3
  - (b) +6
  - (c) +5
  - (d) +2
- (x) The Ecosystem is the smaller unit of:
  - (a) Biosphere
  - (b) Lithosphere
  - (c) Atmosphere
  - (d) Hydrosphere
- (xi) When  $Cl_2$  is passed through water then disinfection is done due to the production of:
  - (a) HCl
  - (b) HOCl
  - (c) NOCl
  - (d)  $HClO_2$
- (xii) Water is purified by:
  - (a) Aeration
  - (b) Coagulation
  - (c) Disinfection
  - (d) All
- (xiii) Which of the following is a not a bacterial diseases?
  - (a) Polio
  - (b) Typhoid
  - (c) Dysentery
  - (d) Diarrhea
- (xiv) Surfactants are organic compounds having polar or hydrophilic groups such as:
  - (a)  $COOH$
  - (b)  $SO_3H$
  - (c)  $NH_4^+$
  - (d) all
- (xv) One liter of gasoline can contaminate ..... Likes of groundwater.
  - (a) 100
  - (b) 1000
  - (c) 1000000
  - (d) 10000
- (xvi) Which of the following is a viral disease?
  - (a) Jaundice
  - (b) Cholera
  - (c) Typhoid
  - (d) paratyphoid
- (xvii) Which non-metallic elements are generally resistant to biological processes unless very dilute?
  - (a) Arsenic
  - (b) selenium
  - (c) both a & b
  - (d) None

(ii) Time: 2:35 Hours

**(I) SUBJECTIVE**

Total Marks Section B and C: 68

Q2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines.

(iii) Section - B (Marks 42) ( $14 \times 3 = 42$ )

- (i) (a) What are components of environment? (02)
- (b) Write any two importances of atmosphere. (01)
- (ii) (a) Differentiate between primary & secondary pollutants? (02)
- (b) What is smog? (01)
- (iii) What are sources of volatile organic compounds (VOCs) in atmosphere? (03)
- (iv) Which conditions must occur to begin the chemical process of photochemical smog development? (03)
- (v) (a) PAN stands for what? (01)
- (b) What is acid rain? (02)
- (vi) What are different sources & environment effects of? (03)
- (i) VOCs
- (ii) PAN
- (vii) How  $O_3$  is decomposed by oxides of nitrogen? (03)
- (viii) (a) How ozone is produced? (02)



- (b) Enlist the possible alternatives of the use of CFCs. (01)
- (ix) (a) Which diseases are caused by live stock? (1.5)
- (b) What is swamp? (1.5)
- (x) (a) What is green Chemistry? (02)
- (b) What is synthetic efficiency? (01)
- (xi) Give principles of green chemistry. (03)
- (xii) (a) How would you avoid from thermal pollution? (02)
- (b) Give two examples of fluoro - chloro carbons? (01)
- (xiii) What is secondary treatment of waste water? (1.5)
- (b) What is primary treatment of water? (1.5)
- (xiv) Briefly discuss the effect of water pollution. (03)
- (xv) (a) What is global warming? (1.5)
- (b) Which factors are playing major role in global warming? (1.5)
- (xvi) Discuss the sources & typical effects of oxides of S as pollutant. (03)
- (xvii)(a) What are the latest predictions about global warming? (02)
- (b) What gases are responsible for greenhouse effect? (01)
- (xviii) What are the effects of ozone layer depletion? (03)
- (xix)(a) What are the important air pollutants? (1.5)
- (b) What should we do to save ozone? (1.5)

**Section - C**

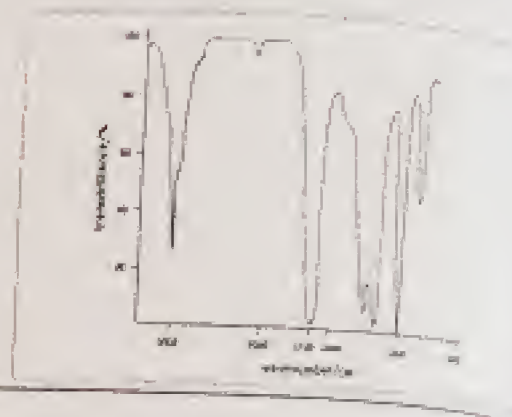
**Note:** Attempt any TWO questions. All questions carry equal marks. (2 × 13 = 26)

1. (a) What are the effects of acid rain? (04)
- (b) Is CO<sub>2</sub> responsible for green house effect? If yes then How? (04)
- (c) How we can control the air pollution caused by hydrocarbons & CO? (05)
2. (a) What is radioactive pollution? What are sources of radioactive pollution & its effects? (05)
- (b) What are control measures for minimizing radioactive pollution? (04)
- (c) Write tow salient principles of green chemistry. (04)
3. (a) What are different treatments of industrial wastewater? (05)
- (b) How following parameters help up to determine the quality of water? (04)
- i) BOD ii) COD
- (c) What are suspended solid & sediments? How they are caused? (04)



## CHAPTER # 24

# ANALYTICAL CHEMISTRY



### Analytical Chemistry

Analytical chemistry is the branch of chemistry that deals with separation and analysis of a sample to identify its components.

The separation is carried out before qualitative and quantitative analysis.

### Qualitative analysis

Qualitative analysis provides the identity of a substance (composition of chemical species).

### Quantitative analysis

Quantitative analysis determines the amount of each components present in the sample.

### Scope of Analytical Chemistry

In analytical chemistry different techniques and instruments used for analysis are studied. The scope of this branch covers food, water, environmental and clinical analysis.

## CLASSICAL METHOD OF ANALYSIS

**Exercise Q3 (I):** What is combustion analysis? Describe its different steps.

### Combustion Analysis and determination of Molecular Formula

The experimental technique by which amount of various elements present in a substance are determined by combustion is called combustion analysis.

- Empirical and molecular formulas for compounds that contain only carbon and hydrogen ( $C_xH_y$ ) or carbon, hydrogen, and oxygen ( $C_xH_yO_z$ ) can be determined by combustion analysis.
- The only products will be  $CO_2$  and  $H_2O$  and these two products of combustion are separately collected

### Procedure:

The steps for this procedure are:

- Weigh a sample of the compound to be analyzed and place it in the apparatus shown in the image below.
- Burn the compound completely. The only products of the combustion of a compound that contains only carbon and hydrogen ( $C_xH_y$ ) or carbon, hydrogen, and oxygen ( $C_xH_yO_z$ ) are carbon dioxide and water.
- The  $H_2O$  and  $CO_2$  are drawn through two tubes. One tube contains a substance that absorbs water, and the other contains a substance that absorbs carbon dioxide.
- Weigh each of these tubes before and after the combustion. The increase in mass in the first tube is the mass of  $H_2O$  that formed in the combustion, and the increase in mass for the second tube is the mass of  $CO_2$  formed.
- Assume that all the carbon in the compound has been converted to  $CO_2$  and trapped in the second tube. Calculate the mass of carbon in the compound from the mass of carbon in the measured mass of  $CO_2$  formed.
- Assume that all of the hydrogen in the compound has been converted to  $H_2O$  and trapped in the first tube. Calculate the mass of hydrogen in the compound from the mass of hydrogen in the measured mass of water.



- If the compound contains oxygen as well as carbon and hydrogen, calculate the mass of the oxygen by subtracting the mass of carbon and hydrogen from the total mass of the original sample of compound.
- Use this data to determine the empirical and molecular formulas

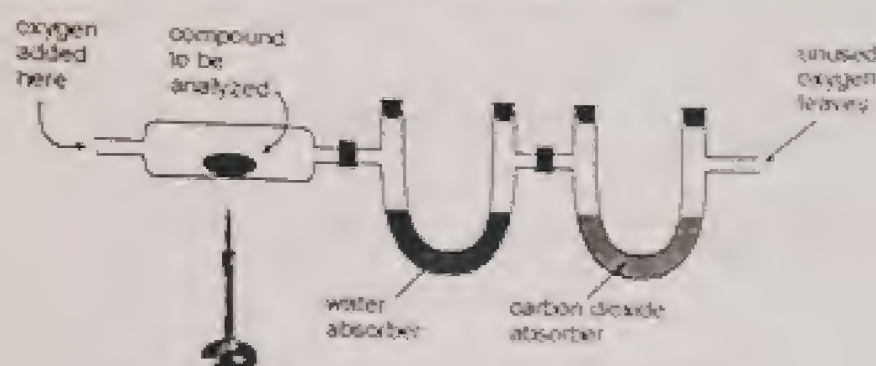


Fig. Apparatus for Combustion Analysis

### Example

Consider a substance called trioxane. Formaldehyde,  $\text{CH}_2\text{O}$ , is unstable as a pure gas, readily forming a mixture of a substance called trioxane and a polymer called paraformaldehyde. That is why formaldehyde is dissolved in a solvent, like water, before it is sold and used.

The molecular formula of trioxane, which contains carbon, hydrogen, and oxygen, can be determined using the data from two different experiments.

- In the first experiment, 17.471 g of trioxane is burned in the apparatus shown above, and 10.477 g  $\text{H}_2\text{O}$  and 25.612 g  $\text{CO}_2$  are formed.
- In the second experiment, the molecular mass of trioxane is found to be 90.079.

### Calculations

We can get the molecular formula of a compound from its empirical formula and its molecular mass. To get the empirical formula, we need to determine the mass in grams of the carbon, hydrogen, and oxygen in 17.471 g of trioxane. Thus, we need to perform these general steps.

- **Step-I:** Determine the grams of carbon, hydrogen, and oxygen from the given data.
- **Step-II:** Determine the empirical formula from the grams of carbon, hydrogen, and oxygen.
- **Step-III:** Determine the molecular formula from the empirical formula and the given molecular mass.

### Step-I

Since it is assumed that all the carbon in trioxane has reacted to form  $\text{CO}_2$ . So the mass of carbon in 17.471 g trioxane is determined by calculating the mass of carbon in 25.612 g  $\text{CO}_2$ .

$$? \text{ g C} = 25.612 \text{ g CO}_2 \left( \frac{1 \text{ mol CO}_2}{44.010 \text{ g CO}_2} \right) \left( \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} \right) \left( \frac{12.011 \text{ g C}}{1 \text{ mol C}} \right) = 6.9899 \text{ g C}$$

Since it is assumed that all the hydrogen in trioxane has reacted to form  $\text{H}_2\text{O}$ . So, the mass of hydrogen in 17.471 g trioxane is determined by calculating the mass of hydrogen in 10.477 g  $\text{H}_2\text{O}$ .

$$? \text{ g H} = 10.477 \text{ g H}_2\text{O} \left( \frac{1 \text{ mol H}_2\text{O}}{18.0153 \text{ g H}_2\text{O}} \right) \left( \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} \right) \left( \frac{1.00797 \text{ g H}}{1 \text{ mol H}} \right) = 1.1724 \text{ g H}$$

Since, trioxane contains only carbon, hydrogen, and oxygen, so the mass of oxygen is determined by subtracting the masses of carbon and hydrogen from the total mass of trioxane.

$$? \text{ g O} = 17.471 \text{ g trioxane} - 6.9899 \text{ g C} - 1.1724 \text{ g H} = 9.309 \text{ g O}$$



**Step-II**

We now calculate the empirical formula.

$$? \text{ mol C} = 6.9899 \text{ g C} \left( \frac{1 \text{ mol C}}{12.011 \text{ g C}} \right) = 0.58196 \text{ mol C} \div 0.5818 \approx 1 \text{ mol C}$$

$$? \text{ mol H} = 1.1724 \text{ g H} \left( \frac{1 \text{ mol H}}{1.00797 \text{ g H}} \right) = 1.1631 \text{ mol H} \div 0.5818 \approx 2 \text{ mol H}$$

$$? \text{ mol O} = 9.309 \text{ g O} \left( \frac{1 \text{ mol O}}{15.9994 \text{ g O}} \right) = 0.5818 \text{ mol O} \div 0.5818 = 1 \text{ mol O}$$

**Step-III**

The empirical formula is  $\text{CH}_2\text{O}$ , which can be used to calculate the molecular formula.

$$\begin{aligned} \text{Empirical formula mass} &= 1(12.011) + 2(1.00794) + 1(15.9994) \\ &= 30.026 \end{aligned}$$

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}} = \frac{90.079}{30.026} \approx 3$$

Molecular formula  $\text{C}_3\text{H}_6\text{O}_3$

**Drawbacks:**

The classical method i.e. combustion analysis is only limited to those organic compounds which contain carbon, hydrogen and oxygen. So there is a need of such methods which explain/find all types of atoms/elements present in an organic compounds. Hence now modern methods are used for this purpose.

**QUICK QUIZ-1**

(1) Give difference between qualitative and quantitative analysis

Qualitative analysis provides the identity of a substance (composition of chemical species).

Quantitative analysis determines the amount of each components present in the sample.

(2) Name the products obtained by complete combustion of hydrocarbon.

The only products of the combustion of a hydrocarbon are carbon dioxide and water.  
e.g.  $\text{CH}_4 + 2\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$

(3) How mass of oxygen is calculated if it also present along with carbon and hydrogen

If the compound contains oxygen as well as carbon and hydrogen, then the mass of the oxygen is calculated by subtracting the mass of carbon and hydrogen from the total mass of the original sample of compound.

(4) Give general steps used to calculate empirical formula

- Determine the percentage composition of each element in a substance.
- Divide the percentage of each element by its atomic mass to get number of gram atoms (moles).
- Divide the moles of each element by the smallest number of moles to get atomic ratios.
- If atomic ratios are not in simple whole number, then multiply with a small suitable number to get whole number ratio.

Thus empirical formula is obtained.

(5) Give drawback of combustion analysis

The classical method i.e. combustion analysis is only limited to those organic compounds which contain carbon, hydrogen and oxygen.



## MODERN METHODS OF ANALYSIS

- Modern chemistry laboratories use sophisticated instruments to find the structure of organic chemicals.
- These instruments are very sensitive and they usually need only very small amounts of the chemical to work on.
- Laboratories in industry and universities are equipped with a range of instruments, but they tend to be very expensive, so you don't find many of them in schools.

### SPECTROSCOPY

#### Spectroscopy:

Spectroscopy involves using instruments to examine the radiation emitted or absorbed by chemicals giving information about their molecular structure.

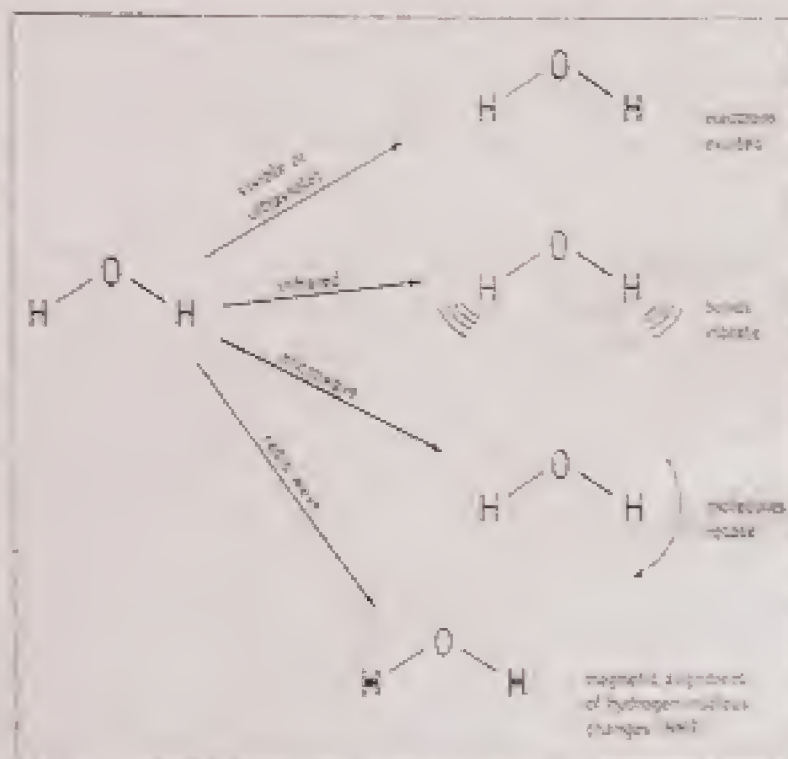
#### Spectroscope:

A spectroscope is an instrument which allows radiation to interact with a sample of a chemical, then analyses the changes.

#### Theory

When electromagnetic radiation, such as light or infrared, shines on a chemical the chemical may interact with the radiation in some way. The commonest example is color. Color is produced when chemicals emit or absorb visible light of a particular frequency. The way a particular chemical interacts with radiation can tell about its molecules and structure.

Different kinds of radiation interact with chemicals in different ways as shown in the figure for water. The effects are given in the table.



#### Types of Spectroscopy

There are many types of spectroscopy. Among these five types of spectroscopy are particularly useful to chemists:

These are: infrared, ultraviolet/visible, nuclear magnetic resonance, atomic emission and absorption, spectroscopy and mass spectroscopy.

Table

How different types of radiation interact with chemicals

Type of radiation	Frequency range /Hz	Effect on molecule	Type of spectroscopy
ultraviolet	$10^{15} - 10^{17}$	excites the electrons	ultraviolet/visible spectroscopy (see below)
visible light	$10^{14} - 10^{15}$	excites the electrons	ultraviolet/visible spectroscopy (see below)
infrared	$10^{11} - 10^{12}$	makes bonds vibrate	infrared spectroscopy (page 365)
microwaves	$10^9 - 10^{11}$	makes molecules rotate	microwave spectroscopy
radio waves	$10^6 - 10^8$	changes the magnetic alignment of the nuclei of some atoms	nuclear magnetic resonance (page 357)

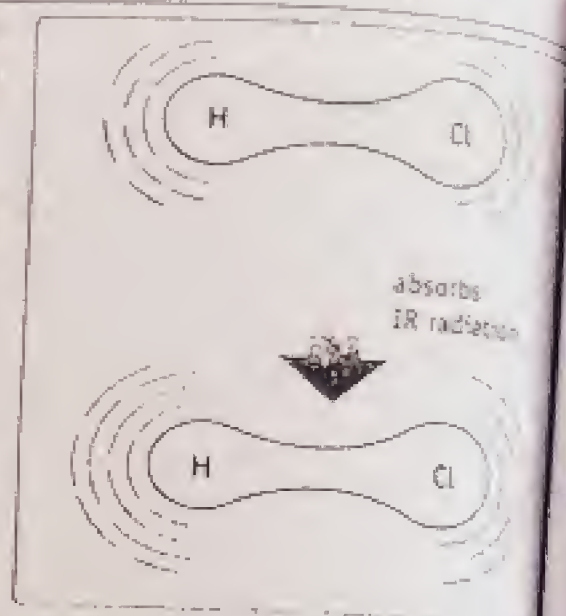


## INFRARED SPECTROSCOPY (IR)

- The molecules absorb infrared (IR) radiation which has a wavelength longer than visible light.
- The commonly used IR radiations have range between about 2500 nm and 25000 nm.

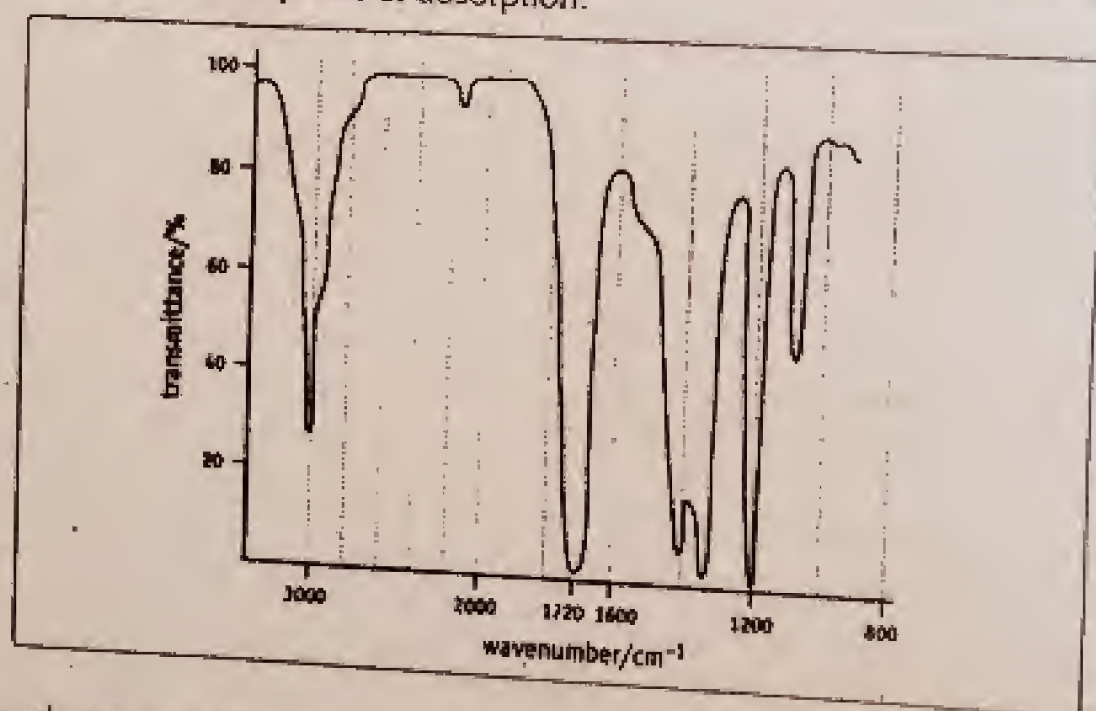
### Theory and Importance:

- The energy of the absorbed IR radiation makes the bonds vibrate as shown in the fig. When the molecule absorbs the radiation the bonds vibrate more energetically.
- Different bonds absorb radiation of different frequencies. The absorbed frequency is the characteristic of a particular bond. Thus, IR absorption can be used to identify the bonds, and therefore, the functional groups in an organic molecule.
- The figure shows that the effect of IR radiations of vibration of HCl. When an HCl molecule absorbs infrared radiation, it vibrates more energetically. The frequency of radiation absorbed is  $7.21 \times 10^{13} \text{ Hz}$ , and this frequency is characteristic of the H-Cl bond.



### Interpretation of IR spectrum:

- The IR spectrometer produces an infrared spectrum on a chart recorder as shown in the fig. The spectrum contains several peaks of absorption.



- There are always some characteristic peaks of absorption which can identify functional groups of a molecule. The characteristic absorption of some common bonds is given in the table.
- Infrared spectra are very useful: they are particularly helpful for identifying the functional groups of an unknown compound.
- In IR spectroscopy the strength of the peak is a characteristic of the bond itself not of the number of bonds present.
- Most of the interesting parts of an IR spectrum are found in the region above about  $1500 \text{ cm}^{-1}$ . It is called the functional group region.
- The peaks below this region are less useful. It is called fingerprint region. Because it is helpful in showing the fingerprint of the compound: the characteristic pattern of its IR spectrum. The fingerprint can be used to compare the compound's spectrum with IR spectra of known compound given in standard reference books.



**Example 1, IR spectrum of Propanone (Acetone):**

The given spectrum is the IR spectrum of propanone (acetone),  $\text{CH}_3\text{COCH}_3$ .

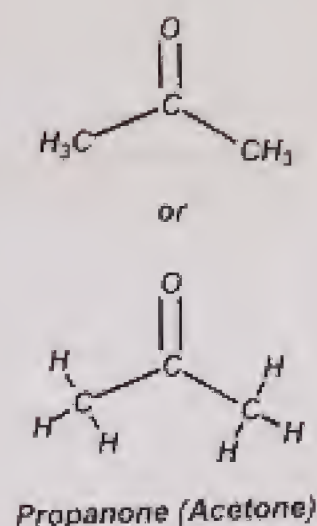
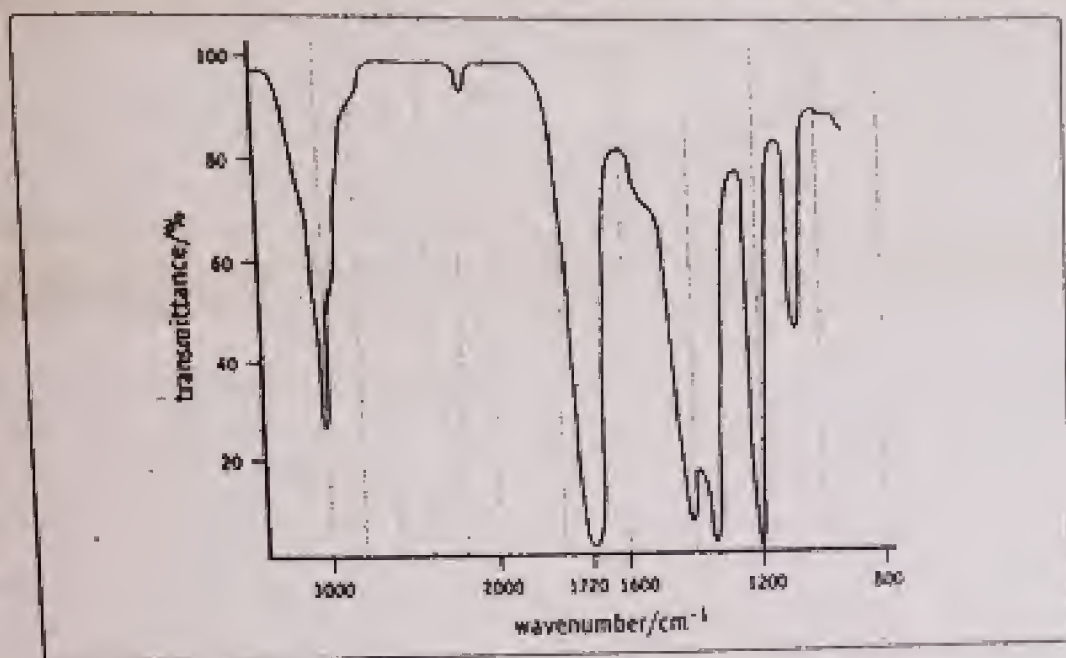


Fig. The infrared spectrum of propanone

- The propanone is a simple molecule with only three types of bond. However, the spectrum is quite complicated. It is because each bond can vibrate in different ways and the vibrations can interact with each other.
- The IR spectrum of propanone consists of two characteristic peaks
  - ✓ The strong peak at about  $1720\text{cm}^{-1}$  corresponds to the  $\text{C}=\text{O}$  bond.
  - ✓ The weaker absorption at  $3000\text{cm}^{-1}$  corresponds to the  $\text{C}-\text{H}$  bond. This peak is weaker even though there are more H atoms in the molecule

**Example 2, IR spectrum of Ethanol:**

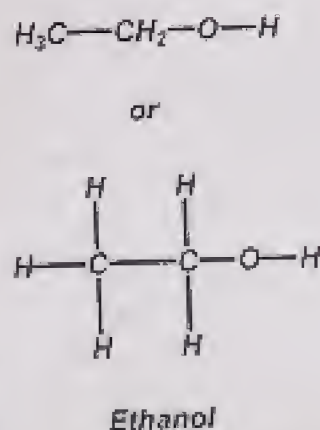
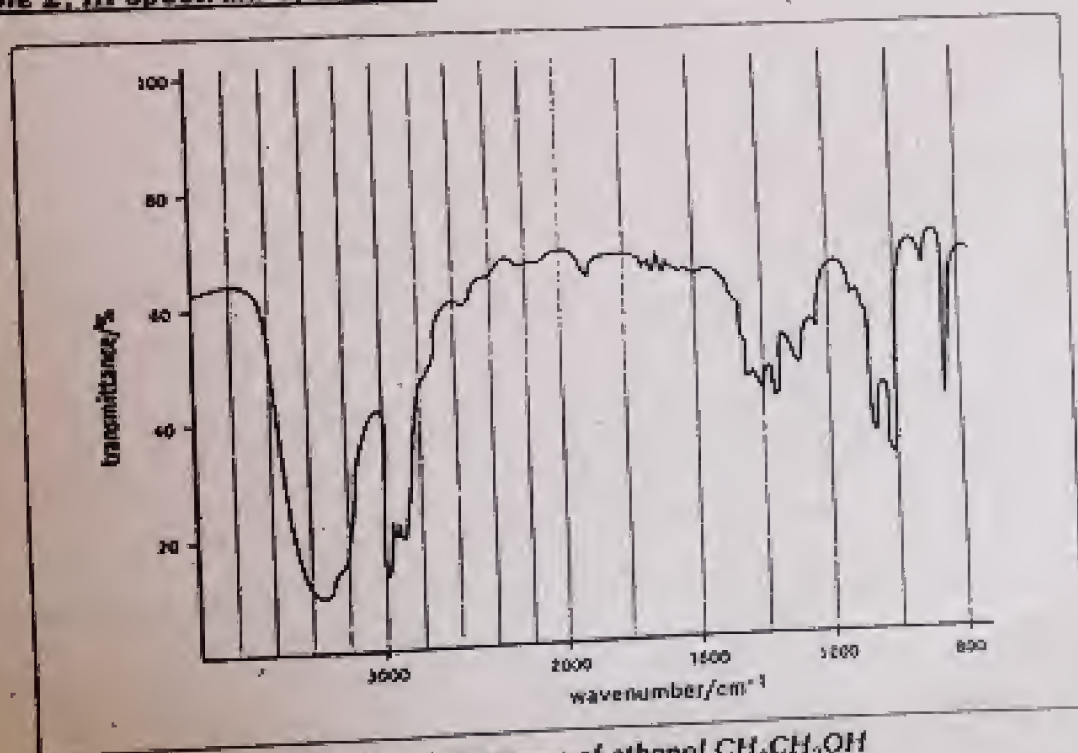


Fig. The infrared spectrum of ethanol  $\text{CH}_3\text{CH}_2\text{OH}$

In the IR spectrum for ethanol following are the characteristic peaks.

- The peak just below  $3000\text{cm}^{-1}$  is from the  $\text{C}-\text{H}$  bonds
- The peak at about  $3400\text{cm}^{-1}$  is from the  $\text{O}-\text{H}$  bond.



## QUICK QUIZ-2

Figure 24.5 shows the IR spectrum of ethanol,  $\text{CH}_3\text{CH}_2\text{OH}$ . Look closely at the spectrum.

(i) What bond gives rise to the peak just below  $3000\text{cm}^{-1}$ ?

This is due to C-H stretching vibration.

(ii) What bond gives rise to the peak at about  $3400\text{cm}^{-1}$ ?

This is due to O-H stretching vibration. The broad peak is due to hydrogen bonding.

## ULTRAVIOLET AND VISIBLE SPECTROSCOPY (UV-Vis)

### Emission Spectrum:

When electrons of a substance are excited by heating or by an electrical discharge, then the substance emits radiations of certain frequencies. It is called emission spectrum.

The radiation may be in the ultraviolet region of the spectrum as well as the visible.

### Examples and Theory:

- When sodium chloride is heated in a flame, it gives a yellow flame color.
- Consider methylene blue (an organic dye). When white light shines on methylene blue, some of the electrons in the dye's molecules become excited. The electrons absorb certain frequencies of light radiation, and change their energy level. The absorbed radiations belong to the red end of the spectrum. If red light is removed from white light, then its color becomes blue. The color of methylene blue can only be noticed if light is shining on it. This is an example of a visible absorption spectrum, where a chemical absorbs certain frequencies of visible radiation.
- Ultraviolet radiation can be absorbed in a similar way. It is not visible but can be detected by instruments. By finding which frequencies have been absorbed chemists can get information about the chemical. Consider an aqueous solute of titanium (III) chloride. This contains the octahedral complex ions,  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , and  $\text{Cl}^-(\text{aq})$  ions. A solution of titanium(III) chloride is violet. An absorption spectrum shows that the solution absorbs most effectively in the green-yellow region of the spectrum figure. Red blue and violet radiations are absorbed less efficiently, so the solute looks violet. Both water and  $\text{Cl}^-(\text{aq})$  are colorless, so the  $\text{Ti}^{3+}(\text{aq})$  ion must be responsible for the color of the solution.

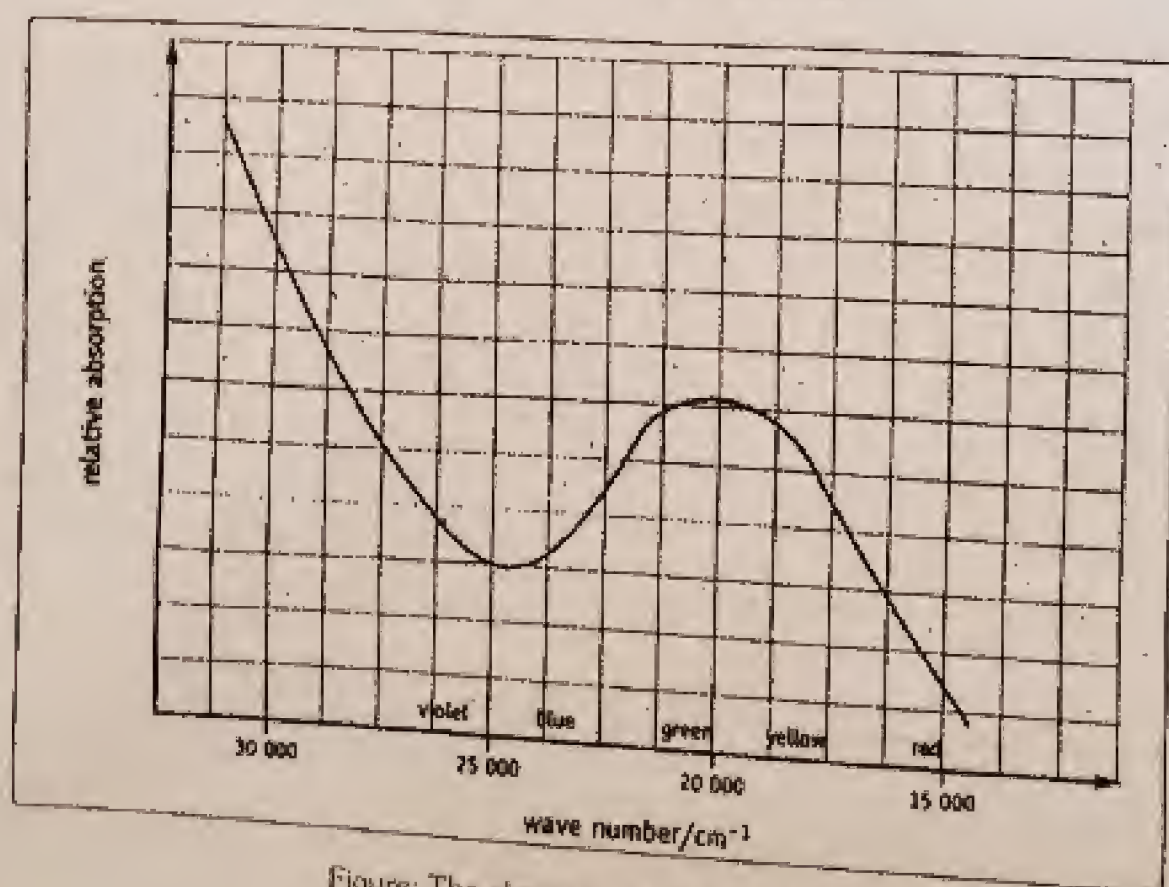


Figure: The absorption spectrum of  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$



### Importance:

By examining the frequencies emitted, chemists can get information about the substance. It particularly gives information about conjugation and extent of conjugation in a substance.

The emission spectrum of hydrogen gave chemists the first clues about the energy levels of electrons in an atom.

Generally, higher the conjugation in a substance, higher will be the wavelength of light that will be absorbed.

### Instrumentation and Working:

In an ultraviolet/visible spectroscope, radiation consisting of a mixture of ultraviolet and visible frequencies is passed through a sample of a compound.

A detector measures the frequencies of absorbed radiations and prints out an absorption spectrum.

The figure shows the ultraviolet/visible absorption spectrum of methylene blue. The horizontal axis shows the wavelengths of radiation absorbed, in nanometers (nm). The vertical axis shows the relative absorbance, i.e., how strongly it is absorbed.

The ultraviolet/visible spectrum of an organic compounds is characteristic of that compound.

The compound can be identified by comparing its spectrum with the spectra of known compound.

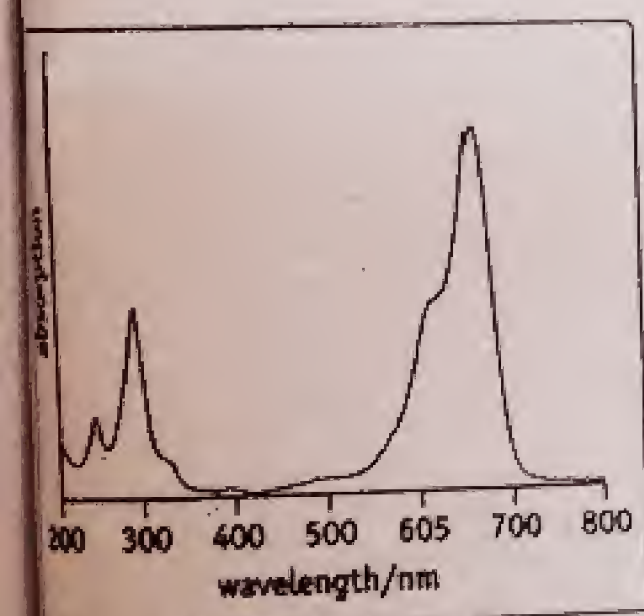


Figure: The visible/UV spectrum of methylene blue

The approximate wavelengths of visible radiation of different colours

Colour	Approximate wavelength/nm
[infrared]	above 700
red	620–700
orange	600–620
yellow	580–600
green	520–580
blue-green	490–520
blue	440–490
indigo	420–440
violet	400–420
[ultraviolet]	below 400

### Note:

UV-Vis spectroscopy is an important technique for the detection of compounds. However other types of spectroscopy particularly infrared and nuclear magnetic resonance, are more useful for determining the structure of an organic compound.



## NUCLEAR MAGNETIC RESONANCE (NMR)

### Theory

- When certain atoms are placed in a strong magnetic field, their nuclei behave like tiny bar magnets. They align themselves with the field. Electrons also behave similarly. Both electrons and protons possess spin and any spinning charge has an associated magnetic field.
- The electrons with opposite spin pair up together. Similarly the protons and neutrons also pair up in a nucleus. Hence, if a nucleus has an even number of protons and neutrons, their magnetic fields cancel out and it has no overall magnetic field. But if the number of protons and neutrons is odd, the nucleus has a magnetic field.
- If the substance is now placed in an external magnetic field, the nuclear magnets line up with the field, just as a compass needle lines up with a magnetic field as shown in the figure.

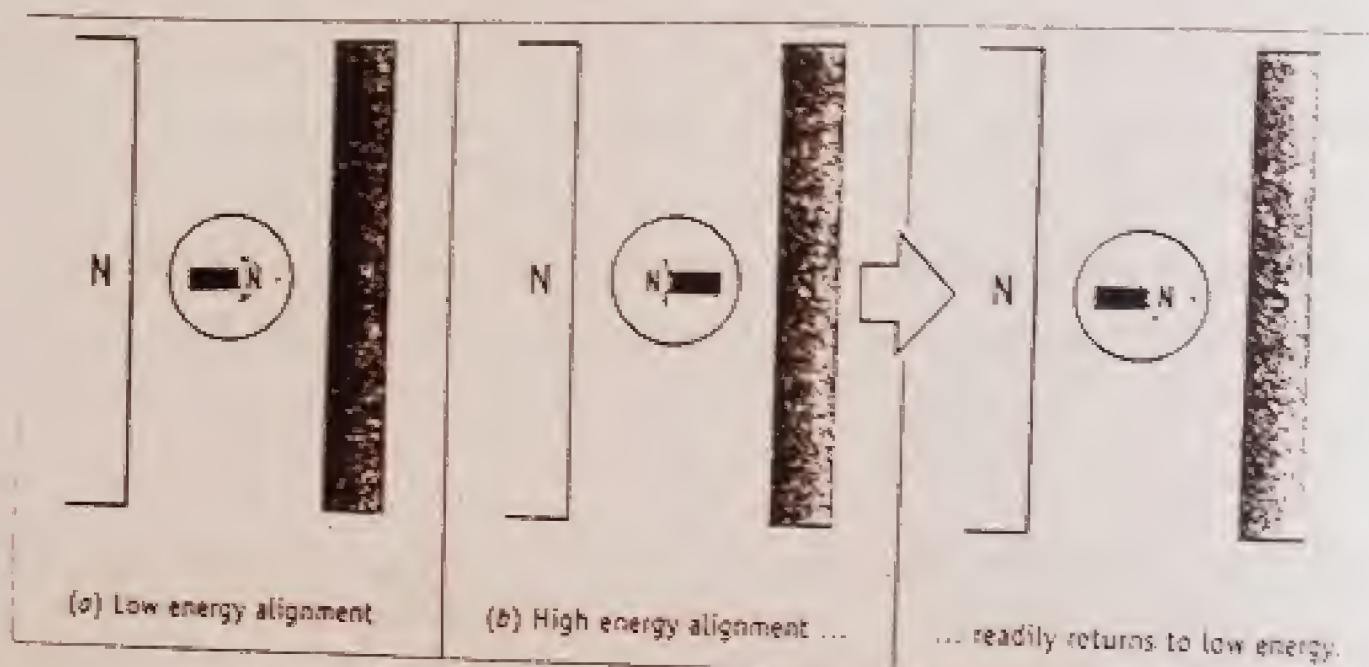


Figure: Alignment of a compass needle in a magnetic field.

- The nuclear magnet can have two alignments of low and high energy as shown in the figure. The nuclear magnet can be changed from low energy to the high energy alignment by supplying energy. This is called spin flipping.

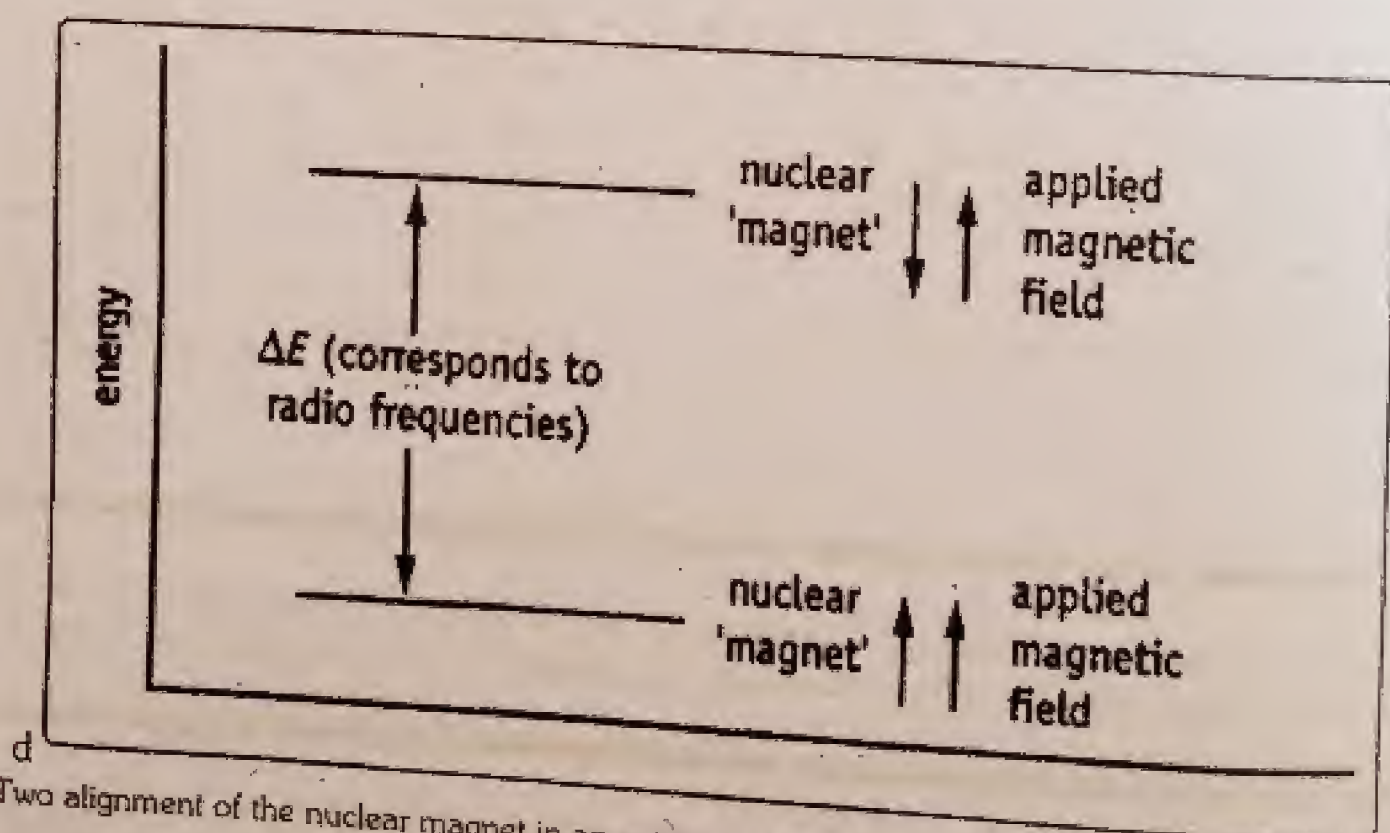


Figure: Two alignments of the nuclear magnet in an external magnetic field. The energy difference between the two orientations is the basis of the technique of NMR.

- The energy required for spin flipping is provided by radio frequency radiations.



- The exact frequency of energy depends on the environment of the nucleus. i.e., it depends on the other nuclei and electron in its neighborhood.
- Hence, when a sample is placed in a strong magnetic field, different protons in a molecule absorb different frequencies of radiation. This technique is called nuclear magnetic resonance (NMR) spectroscopy.
- The result is recorded in the form of an NMR spectrum which contain signals of different protons. In NMR spectrum the chemical shift values are present on X-axis and intensity of absorption on Y-axis.

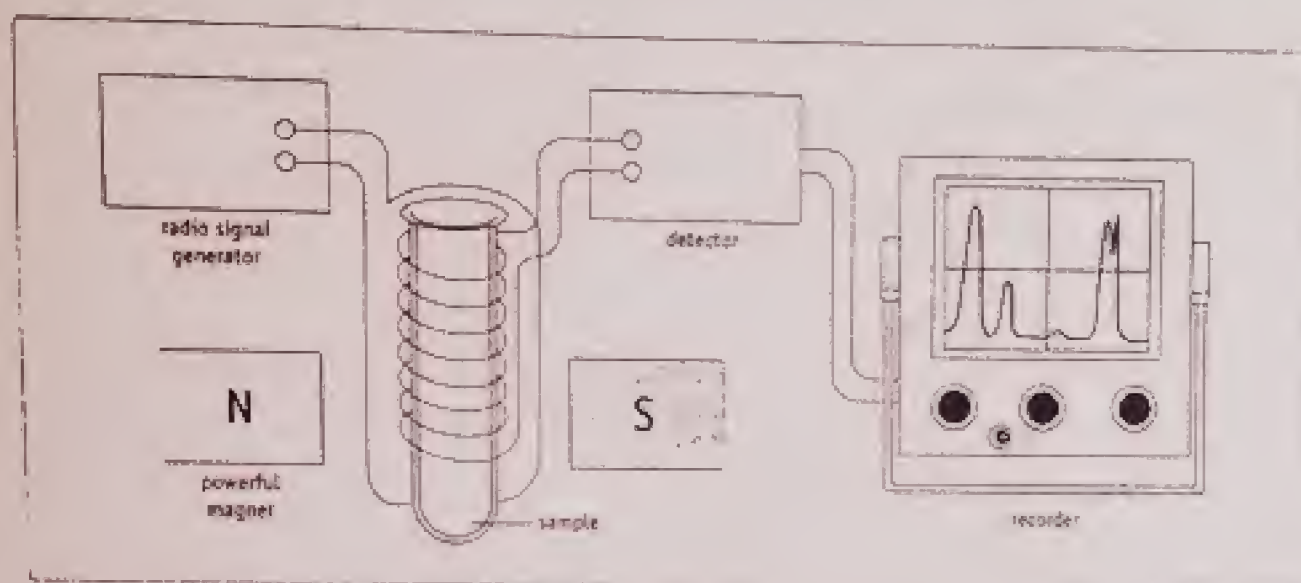


Figure: A simplified NMR spectrometer. The sample is dissolved in a solvent such as  $^2\text{H}_2\text{O}$  or  $\text{CCl}_4$  which does not have nuclear magnetic properties.

### IMPORTANCE OF NMR

- The technique of NMR is particularly useful for identifying the number and type of hydrogen atoms ( $^1\text{H}$ ) in a molecule.
- It is also used to find the position of carbon atoms. The common isotope of carbon,  $^{12}\text{C}$  does not have a nuclear magnet but natural carbons contains 1% of the  $^{13}\text{C}$  isotope which does show magnetic behavior and can be identified using NMR.

**Exercise Q3 (iv):** What is meant by the term chemical shift of a particular proton in NMR spectroscopy? Also draw the splitting pattern of protons in NMR spectrum of ethyl alcohol (For ethyl alcohol see Example 2 below).

### CHEMICAL SHIFT


The separation of a signal in NMR spectrum from a reference point is called chemical shift.

It is denoted by  $\delta$ .

- The H atoms in a particular type of environment have similar positions in the NMR spectrum. Normally this position is measured as a chemical shift, form a fixed reference point. The reference point normally used is the absorption of a substance known as TMS. The chemicals shift of TMS is set at zero.
- TMS stands for tetramethylsilane,  $\text{Si}(\text{CH}_3)_4$ . This non-toxic and uncreative substance is chosen as the NMR reference because its protons give a single peak that is well separated from the peaks found in the NMR spectra of most organic compounds.

The following table gives the chemical shifts for some common proton environments.



Type of proton	Chemical shift, $\delta$ , in region of
$R-CH_3$	0.9
$R-CH_2-R$	1.3
$\begin{array}{c} R \\   \\ R-CH-R \end{array}$	2.0
$\begin{array}{c} -C-CH_2- \\    \\ O \end{array}$	2.3
$-O-CH_3$	3.8
$-O-CH_2-R$	4.0
$-O-H$	5.0
	7.5
$\begin{array}{c} -C=O \\   \\ H \end{array}$	9.5
$\begin{array}{c} -C=O \\   \\ O-H \end{array}$	11.0

### Intensity of Absorption

In NMR spectrum, the intensity of absorption on Y-axis gives the number of nuclei present in a particular environment. The relative ratio of area under each peak is measured by an integrator present in NMR spectrometer.

### INTERPRETATION OF NMR SPECTRUM

#### Example 1:

- Consider the NMR spectrum of ethylbenzene  $C_6H_5CH_2CH_3$  as shown in the figure.

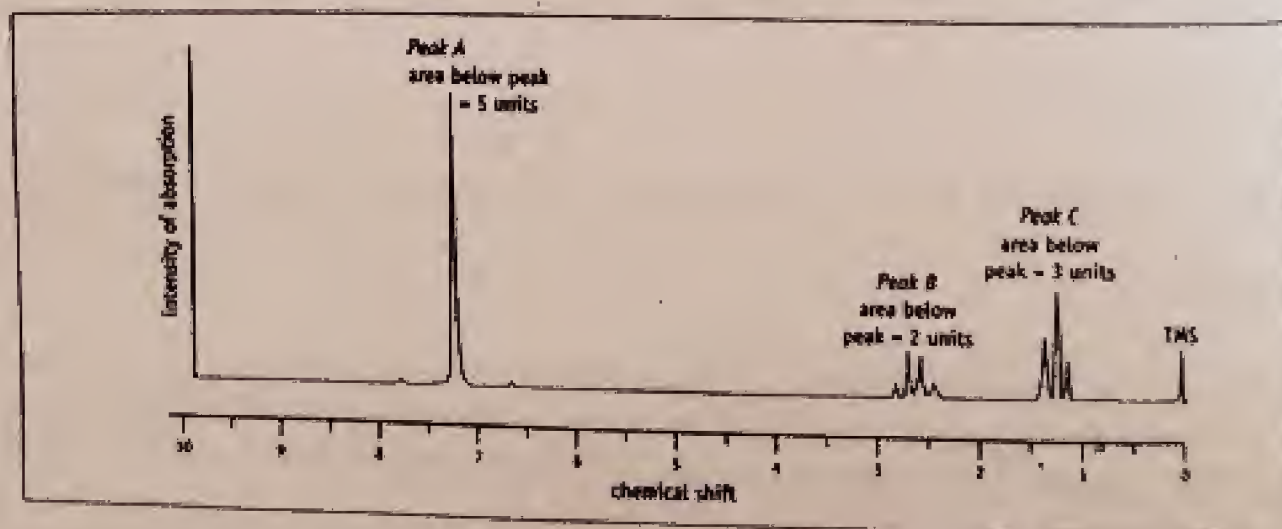


Figure: The proton NMR spectrum of ethylbenzene,  $C_6H_5CH_2CH_3$

- This is a proton NMR spectrum: the frequencies correspond to the absorption of energy by  $^1H$  nuclei which are protons. There are three major peaks of differing heights.



- Each peak corresponds to H atoms in a different molecular environment. This area under each peak is proportional to the number of that type of H atom in the molecule.
- The largest peak (A) corresponds to the 5 H atoms in  $C_6H_5$ , the benzene ring.
- The second largest (C) corresponds to the 3 H atoms in the  $-CH_3$  group.
- The third peak (B) corresponds to the 2 H atoms in the  $CH_2$  group.

**Example 2:**

- The following figure shows a simplified proton NMR spectrum for ethanol,  $CH_3CH_2OH$ .
- It has been simplified by removing some of the detail, so the peaks appear single.
- The peak for TMS is also present.
- The integrated trace is also shown which gives the relative areas under each of the peaks.

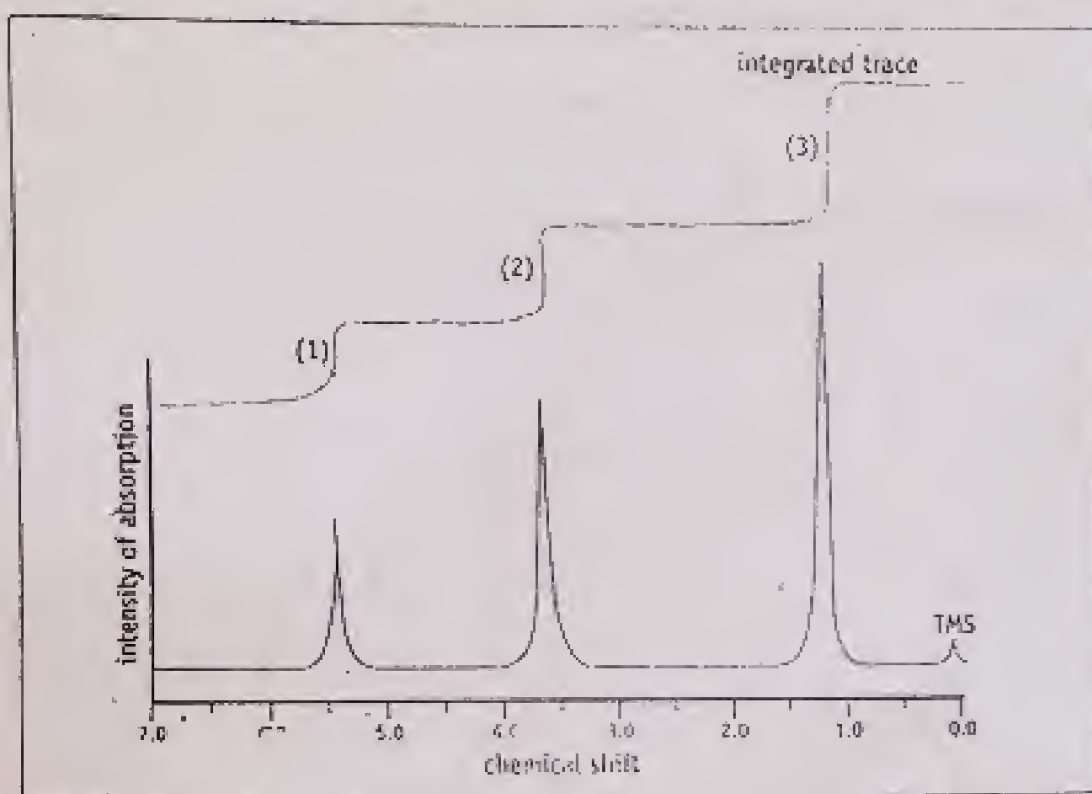


Figure: A simplified proton NMR spectrum for ethanol,  $CH_3CH_2OH$ . The integrated trace shows that areas under the peaks are in the ratio 1:2:3

From the table of chemical shift values, the spectrum of ethanol can be interpreted as

- The largest peak (3) corresponds to the 3 H atoms in  $-CH_3$ .
- The second largest peak (2) corresponds to the 2 H atoms in the  $-CH_2$  group.
- The third peak (1) corresponds to the 1 H atoms in the  $-OH$  group.

**QUICK QUIZ-3**

(I) Use table to identify each of the peaks in figure (NMR spectrum of ethanol)

Approximate chemical shift values ( $\delta$ values)	Nature of proton
About 5.4	Hydroxyl protons (OH)
About 3.5	Methylene protons ( $CH_2$ )
About 1.3	Methyl protons ( $CH_3$ )



**(ii) Explain the relative areas under the peaks**

The ratio of relative height of integrated trace in the NMR spectrum is

Peak (1) : Peak (2) : Peak (3)  
1 : 2 : 3

Thus,

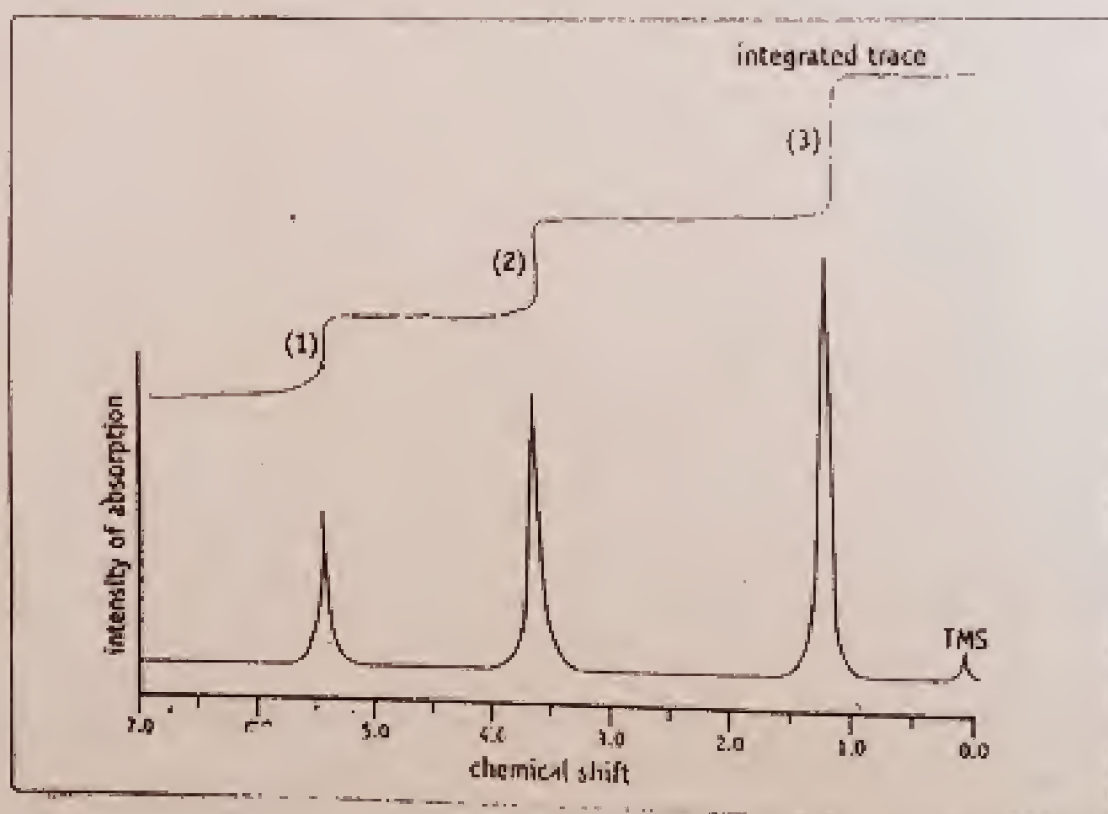
- Peak (1) corresponds to one proton (due to OH)
- Peak (2) corresponds to two protons (due to CH<sub>2</sub>)
- Peak (3) corresponds to three protons (due to CH<sub>3</sub>)

**SPIN-SPIN COUPLING:**

In NMR, the magnetic interaction of neighboring nuclei with each other is called spin-spin coupling.

In NMR, the splitting of signal of a particular nucleus due to spin-spin coupling with neighboring nuclei is called spin-spin splitting.

Consider the simplified NMR spectrum of ethanol as shown below.



It shows three single peaks.

- The smallest peak corresponds to the single OH proton
- The middle peak corresponds to the two CH<sub>2</sub> protons.
- The largest peak corresponds to the three CH<sub>3</sub> protons.

A detailed high-resolution spectrum of ethanol shows that the CH<sub>2</sub> and CH<sub>3</sub> peaks are in fact split into a number of subsidiary peaks as shown in the figure below. This splitting is caused by spin-spin coupling between protons on neighboring carbon atoms.



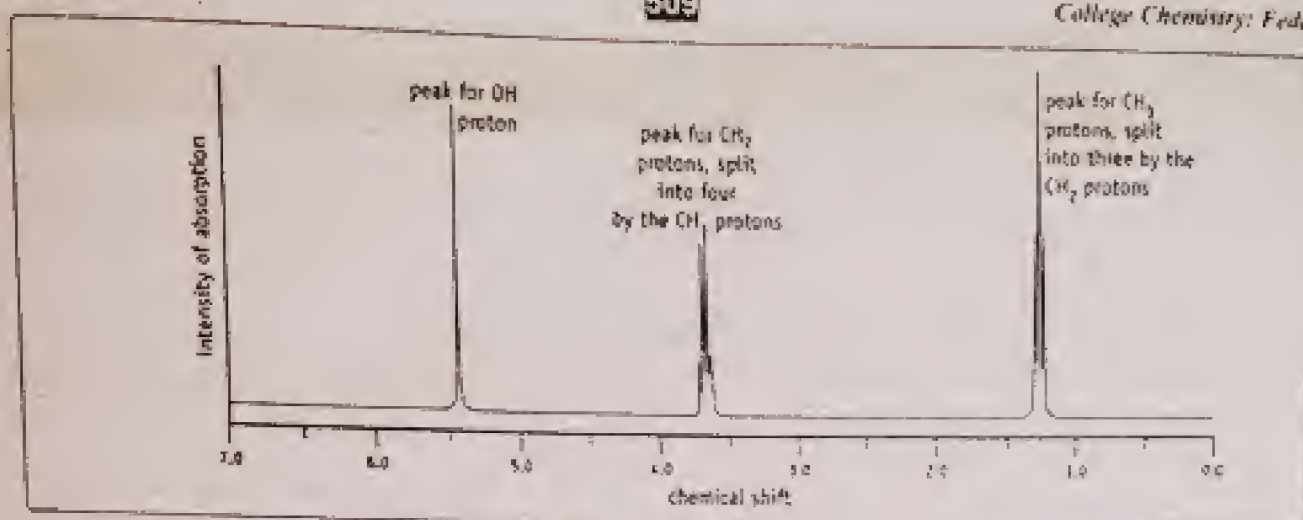


Figure: A detailed high-resolution NMR spectrum for ethanol

### Explanation of spin-spin coupling:

- One of the carbon atoms in ethanol has two protons on it ( $\text{CH}_2$ ). The other has three protons on it ( $\text{CH}_3$ ). Consider  $\text{CH}_3$  protons which act like tiny magnets. When the external magnetic field is applied, these three tiny magnets can arrange themselves in four different ways.

- (i) All three aligned with the magnetic field
- (ii) All three aligned against the magnetic field
- (iii) Two aligned with the field and one aligned against it
- (iv) One aligned with the field and two aligned against it.

Each of these four arrangements gives a slightly different overall magnetic field. So, each different field interacts with the neighboring  $\text{CH}_2$  protons slightly differently.

Thus, these  $\text{CH}_2$  protons give four different peaks very close to one another. These peaks are called a **quartet**.

- Similarly the two protons on the  $\text{CH}_2$  group can arrange themselves differently in the external magnetic field. This time there are three different arrangements.

- (i) All two aligned with the magnetic field
- (ii) All two aligned against the magnetic field
- (iii) One aligned with the field and one aligned against it

Each of these different fields interacts with the neighboring  $\text{CH}_3$  protons slightly differently.

Thus, these  $\text{CH}_3$  protons give three different peaks very close to one another. These three peaks are called **triplet**.

### General rule:

A group carrying 'n' protons will cause the protons on a neighboring group to split into 'n + 1' peaks.

Hence, a high-resolution spectrum can be interpreted as

- Use the position of each overall peak to identify the type of protons causing the peak
- Use the integrated trace to find the number of each type of proton
- Use the n+1 rule above to get information about the number of protons on neighboring groups.



## QUICK QUIZ-4

(1) **Which type of nucleus has magnetic field?**

If a nucleus has an even number of protons and neutrons, their magnetic fields cancel out and it has no overall magnetic field. But if the number of protons and neutron is odd then the nucleus has a magnetic field.

(2) **What happens when a magnetic nucleus is placed in magnetic field?**

If a magnetic nucleus is placed in an external magnetic field, the nuclear magnets line up with the field. The nuclear magnet can have two alignments.

- One is of low energy, which is along the external magnet field and
- Other is of high energy, which is against the external magnetic field.

(3) **What is nuclear magnetic resonance spectroscopy?**

It is an analytical technique used to find the nature of nuclei having magnetic moment (e.g. protons) in the presence of external magnetic field.

The nuclei which have magnetic moment can take up two orientations in external magnetic field. One is of low energy and the other is of high energy. The low energy state can be converted into high energy state by supplying energy from the radio frequency region. The exact frequency of energy depends on the environment of the nucleus. Hence, different protons in a molecule absorb different frequencies of radiation and thus they can be identified.

(4) **What information is obtained from NMR spectrum?**

In NMR spectrum, different peaks are present. These peaks give two information.

- The position of peak on X-axis gives the nature of nuclei present in a particular environment.
- The intensity of absorption on Y-axis gives the number of nuclei present in a particular environment.

(5) **What information are obtained from numbers of peaks and area under peaks in NMR spectrum?**

- The number of peaks gives the types of nuclei in different environment
- The area under peaks gives the number of nuclei in a particular environment.

(6) **What is NMR reference?**

In NMR spectrum, the position of a particular peak is measured as a chemical shift from a fixed reference point. The reference point normally used is the absorption of a substance known as Tetramethylsilane (TMS). The chemical shift of TMS reference is set at zero.

(7) **Why splitting of peaks occur?**

In NMR, the splitting of signal of a particular nucleus due to spin-spin coupling with neighboring nuclei is called spin-spin splitting.

Let there is a particular nucleus having magnetic moment in a molecule. The magnetic nuclei on neighbouring atoms may have different magnetic field due to their different alignments. So, each neighboring different field interacts with a particular nucleus slightly differently. Thus, the signal of a particular nucleus is split up.

**Exercise Q3 (vi):** What is the basic principle of Atomic Absorption Spectroscopy? Describe the instrumentation used.

## ATOMIC EMISSION SPECTROSCOPY (AES)

In atomic emission spectroscopy electronic transitions occurs in atoms. It is done by an excitation source like flames sparks. It is related to atoms and shows the characteristic radiation produced when atoms are excited. The atoms emit radiations in the form of discrete wavelengths of light, called spectral lines while returning to the lower energy states.



**Principle**

The source vaporizes the sample and causes electronic excitation of elementary particles in the gas. Excited molecules in the gas phase emit band spectra. Thus, a molecule in an excited state of energy,  $E_2$  undergoes a transition to a state of lower energy  $E_1$  and a photon of energy  $h\nu$  is emitted where

$$E_2 - E_1 = h\nu$$

In each electronic state a molecule may exist in a number of vibrational and rotational states of different energies.

**Advantages of Emission Spectroscopy**

Emission method is extremely important in analysis

- (1) This technique is highly specific
- (2) This method is extremely sensitive. With this technique all metallic elements can be detected even if they are present in very low concentration.
- (3) Even metalloids have been identified by this technique.
- (4) This analysis can be performed either in solid or liquid state with almost equal convenience.
- (5) This technique requires minimum sample preparation as a sample can be directly introduced into the spark.
- (6) The technique provides results very rapidly. If automated, time required is just 30 sec to one minute.
- (7) This method has been used for a wide variety of samples like metals, alloys, paints, geological specimen, environmental and biological samples.

**Disadvantages of Emission Spectroscopy**

- (1) The equipment is costly and wide experience is required for its successful handling and interpretation of spectra.
- (2) Recording is done on a photographic plate which takes some time to develop, print and interpret the results.
- (3) Radiation intensities are not always be reproducible.
- (4) Relative error exceeds 1 to 2 %.
- (5) The accuracy and precision are not high.

**Applications:**

- (1) Emission spectroscopy has been employed in determining the impurities of Ni, Mn, Cr, Si, Al, Mg, As Sn, Co, V, Pb, Bi, P and Mo in iron and steel in metallurgical processes.
- (2) Alloys of Zn, Cu, Pb, Al, Mg and Sn have been analyzed.
- (3) Lubricants oils have been analyzed for Ni, Fe, Cr, Mn, Si Al and so on. If the concentration of metal in lubricating oil has increased during use, it indicates excessive wear and tear need for engine overhaul.
- (4) In petroleum industry oil is analyzed for V, Ni, Fe the presence of which makes fuel poor.
- (5) Solid samples and animal tissues have been analyzed for several elements including K, Na, Ca, Zn, Ni, Fe and Mg etc.
- (6) Emission spectroscopy has been used to detect 40 elements in plants and soil. Thus metal deficiency in plants and oil can be diagnosed.
- (7) The following materials have been analysed by emission spectroscopy:
  - (i) Trace and major constituents in ceramics.
  - (ii) Traces of Co, Ni, Mo and V in Graphite.
  - (iii) Trace metal impurities in analytical reagents.
  - (iv) Trace of Ca, Cu, Zn in blood.
  - (v) Zinc in pancreatic tissues.



## QUICK QUIZ-5

### 1) Define atomic emission spectroscopy

In atomic emission spectroscopy electronic transitions occurs in atoms. It is done by an excitation source like flame or spark. The excited atoms emit radiations in the form of discrete wavelengths of light called spectral lines while returning to the lower energy states. The measurement of radiations emitted by an element is called atomic emission spectroscopy.

### 2) What is meant by excitation of molecule

When a substance absorbs energy, electronic excitation of elementary particles occurs from low energy state to high energy state. This is called excitation of molecule. When excited particles return to their low energy state, they emit radiations and thus an emission spectrum is produced.

### 3) Name those elements which can analyze by emission spectroscopy

The elements which can be analyzed by emission spectroscopy are:  
Ni, Mn, Cr, Si, Al, Mg, As, Sn, Co, V, Pb, Bi, Mo, Zn, Cu, Fe, Na, K, Ca etc.

### 4) How emission spectroscopy apply in metallurgy

Emission spectroscopy has been employed in determining the impurities of Ni, Mn, Cr, Si, Al, Mg, As, Sn, Co, V, Pb, Bi, Fe and Mo in iron and steel in metallurgical processes.

## ATOMIC ABSORPTION SPECTROSCOPY (AAS)

The technique has been particularly useful in the determination of trace metals in liquids. The versatility of AAS can be realized from the fact that 60-70 elements have been analyzed by this method in concentrations as low as 1 ppm. The greatest advantage of AAS is the analysis of one metal in the presence of another metal thus saving time and eliminating error.

### Quick Quiz-6 (1): Give principle of atomic absorption spectroscopy

#### Principle of AAS:

Atomic absorption spectroscopy involves the study of the absorption of radiant energy. The common source of radiant energy is the visible light by neutral atoms in the gaseous states. If light of the resonance wavelength passes through a flame containing the atoms, then part of the light will be absorbed. The extent of absorption is proportional to the number of ground state atoms present in the flame.

### Quick Quiz-6 (2): Give few application of atomic absorption spectroscopy

#### Applications of Atomic Absorption Spectroscopy (AAS)

- (1) The AAS technique has become the most powerful tool of analysis. The method is well-suited to the analysis of a substance at low concentration.
- (2) It has several advantages over conventional absorption or emission spectroscopic methods.
- (3) AAS methods are highly specific, hence analysis of a metal from a complex mixture is possible and a high energy source needs not be employed.
- (4) The technique is firmly established in analytical chemistry, ceramics mineralogy, biochemistry, metallurgy, water supplies and soil analysis.

## QUICK QUIZ-6

### (1) Give principle of atomic absorption spectroscopy

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### (2) Give few application of atomic absorption spectroscopy

Page 512



Exercise Q3 (vii): What is the basic principle of Mass Spectrometer? How does it work?

## MASS SPECTROMETRY (MS)

The mass spectrometer is an instrument which turns atoms and molecules into ions and measure their mass.

- In 1919, Aston invented the mass spectrometer. This gave chemists a reliable and accurate method of comparing the relative masses of atoms.
- At one time, the relative masses of atoms were known as atomic weights, but nowadays we refer to them as relative atoms masses.

### Basic Principle:

The basic idea of a mass spectrometer can be demonstrated using the apparatus shown in figure. Wooden balls of different sizes but with identical iron cores, roll down a sloping plane. At the bottom of the slope a powerful magnet attracts the iron cores and the moving balls are deflected.

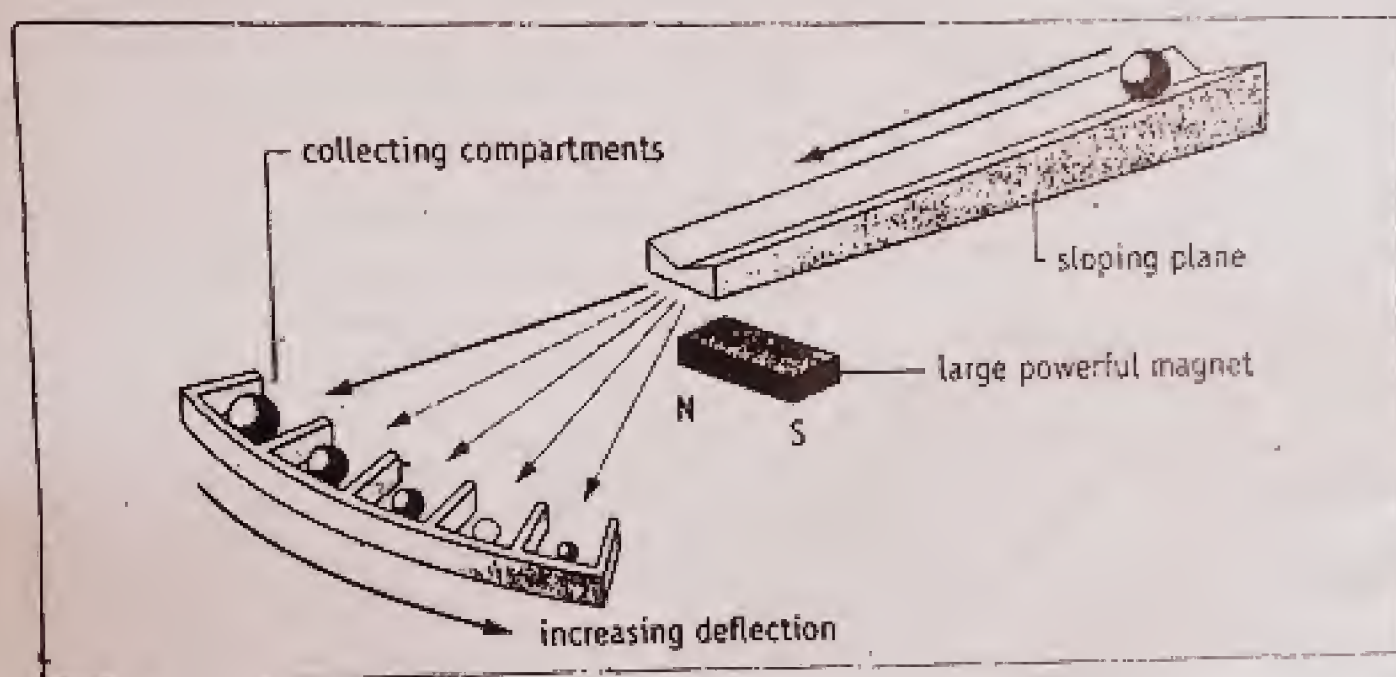


Figure: A simple model to illustrate the working of a mass spectrometer.

- As the balls have identical iron cores, they are all attracted equally by the magnet. But the smaller balls are lighter, therefore they are deflected the most. The balls collect in different compartments depending on their mass. All balls of the same mass collect in the same compartment. Using this simple apparatus, it is possible to separate the different sized balls according to their mass and to find the relative numbers of each present.
- A real mass spectrometer works in a similar fashion to this simple model. It separates atoms according to their mass and shows the relative numbers of the different atoms present. Before the atoms can be deflected and separated, they must be converted to positively charged ions.

## QUICK QUIZ-7

(1) Why does the magnet have the same attraction for all the balls?  
Since the balls have identical iron cores, they are all attracted equally by the magnet.

(2) Which size of ball will be deflected the most? Why?  
The smaller balls are lighter, therefore they are deflected the most.



## Mass Spectrometer Working

The mass spectrometers have five main stages.

1. **Vaporization** – the sample of elements is vaporized.
2. **Ionization** – positive ions are obtained from the vapor.
3. **Acceleration** – the positive ions are accelerated by an electric field.
4. **Detection** – the ions are detected and a record is made.
5. **Recording** – the result is recorded as mass spectrum.

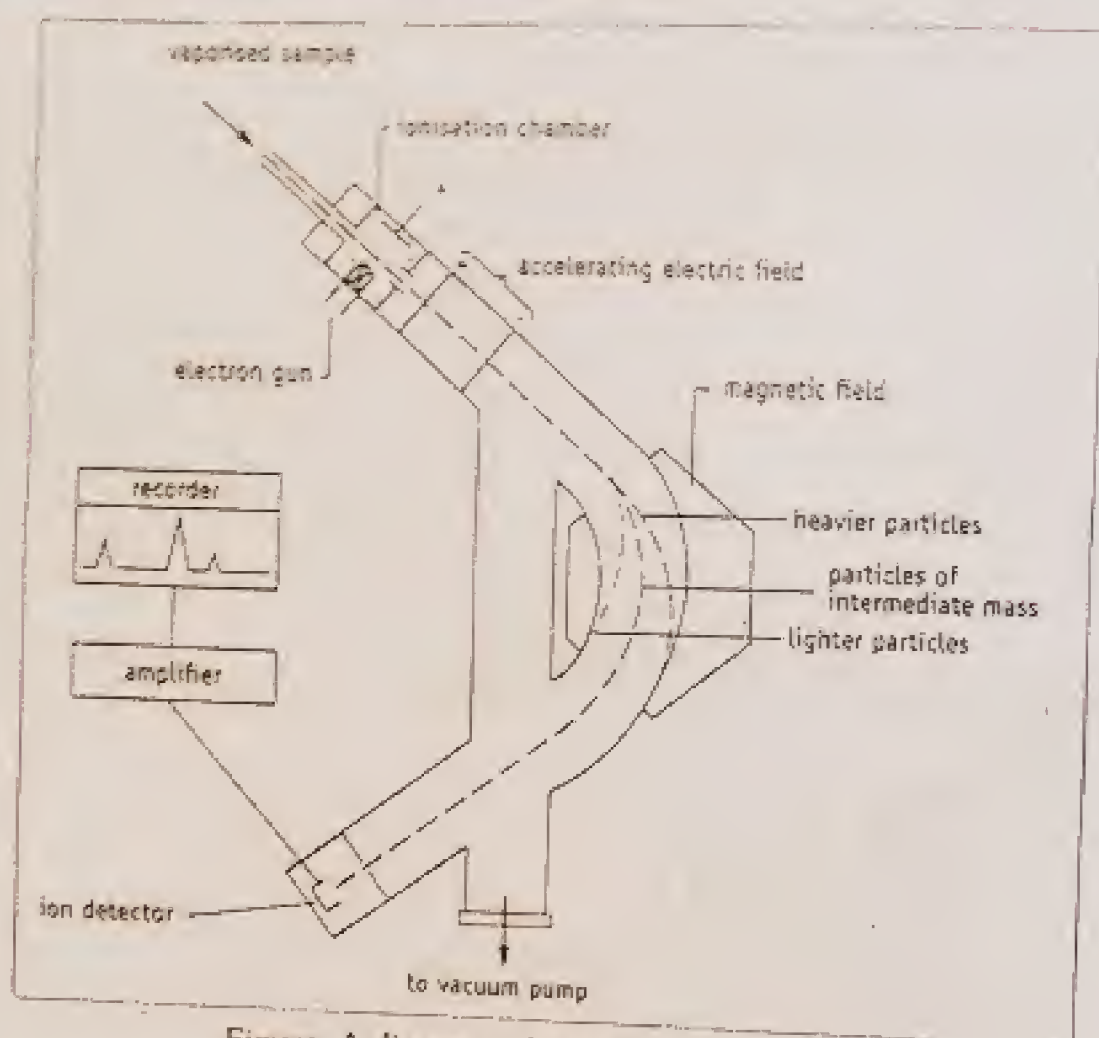


Figure: A diagram of a mass spectrometer.

## Instrumentation and Working

It can be explained as follows

### 1 – Vaporization

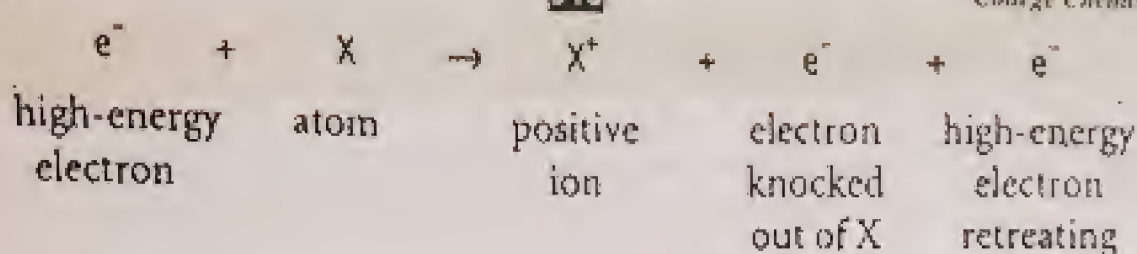
- Gases, liquids and volatile solids are injected into the instrument just before the ionization chamber.
- Less volatile solids must be preheated to vaporize them.

### 2 – Ionization

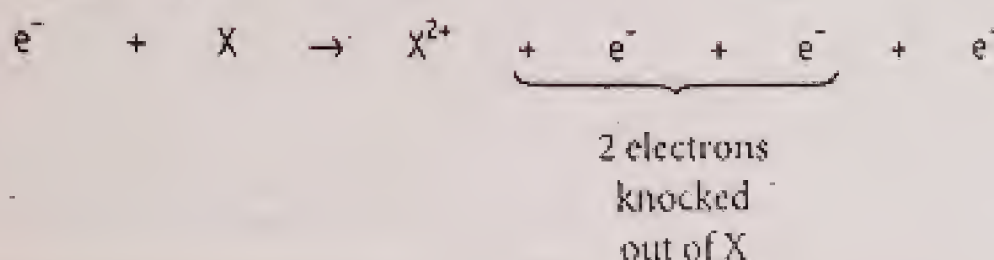
- After vaporization the elements pass into the ionization chamber.
- Here atoms of the elements are bombarded with a stream of high energy electron.
- This causes ionization. One or occasionally two electron are knocked out of the atoms leaving positive ions.

### Example





or occasionally



### 3 - Acceleration

- These positive ions such  $X^+$  and  $X^{2+}$  now pass through holes in parallel plates.
- An electric field is applied to accelerates the ions into the instrument towards the magnetic field.

### 4 - Deflection

- As the ions pass through the magnetic field, they are deflected according to their mass and their charge.
- The particles can only pass through the instrument if they are positively charged.

### 5 - Detection

- If the accelerating electric field and the deflecting magnetic field are constant, ions of only one particular mass/charge ratio will hit the ion detector at the end of the apparatus.
  - ✓ Ions of smaller mass/charge ratio will be deflected too much.
  - ✓ Ions of greater mass/charge ratio will be deflected too little.
- The ion detector is usually linked through an amplifier to a recorder.
- As the strength of the magnetic field is slowly increased ions of increasing mass will be detected and mass spectrum is traced out by the recorder as shown in the figure.

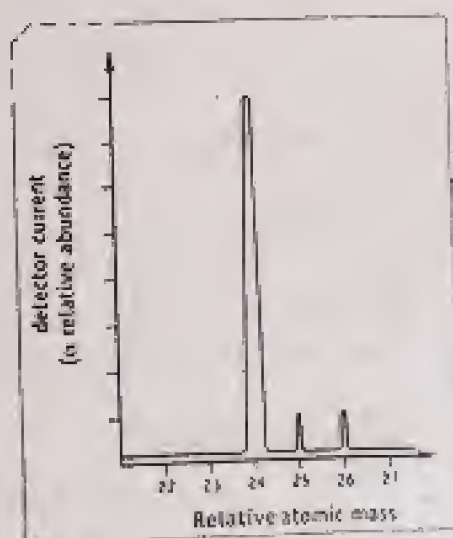


Figure: A mass spectrometer trace for naturally occurring magnesium

- The relative heights of the peaks in the mass spectrum give a measure of the relative amounts of the different ions present.
- In practice a reference peak using a known substance is first obtained on the mass spectrum the relative masses of other particles can then be obtained by comparison with this.



## QUICK QUIZ-8

Look closely at figure 24.15

(1) **How many different ions are detected in the mass spectrum of naturally occurring magnetism?**

Since, there are three peaks in the mass spectrum, therefore, three different ions are detected.

(2) **What are the relative masses of these different ions?**

The position of peaks shows that the relative masses are 24, 25 and 26.

(3) **What are the relative proportions of these different ions?**

The ions with relative mass 24 is most abundant. The ions with relative masses 25 and 26 have comparatively less abundance. However, both these have almost equal abundance.

## SOCIETY, TECHNOLOGY AND SCIENCE

### FORENSIC CHEMISTRY

**Forensic chemistry is the application of chemistry to criminal investigation.**

- It deals with criminal investigation, in the laboratory analysis of forensic evidence.
- It also develops the analytical skills required for other areas of civil law such as environmental pollution, accident investigation and product liability.
- Analytical measurements are essential to everyday life, required to determine the composition and control the quality of many products, to protect the environment and to monitor health.
- Thus, analytical Chemistry is important not only in chemistry, but also in fields such as biochemistry and the forensic, food, environmental and pharmaceutical sciences.
- Forensic chemistry is the application of analytical chemistry to the law and involves the examination of physical traces, such as body fluids, bones, fibres and drugs.
- The success in analytical chemistry requires the ability to make rigorous measurements, an appreciation of the principles and practice of modern instrumentation, and a problem-solving approach.

#### Abilities of a Forensic Chemist

- The forensic chemist requires a strong background in chemical analysis and problem solving skill and must be able to effectively communicate the results of laboratory analysis in reports and in the courtroom.
- The forensic chemist must have a strong theoretical and experimental background in analytical chemistry as well as in problem solving skills.
- Forensic chemists must have good attention to detail and superior problem-solving skills.
- They need critical thinking abilities to solve crime puzzles based on fragmentary evidence.
- Forensic chemists must take accurate notes and make accurate records of their findings. They need strong writing skills to produce clear reports on highly technical subjects so that others can understand.

### CHEMICAL INSTRUMENTATION AND TECHNOLOGY

- Chemical instruments are used extensively in research and development activities, laboratories being one of the major users.
- Use of chemical instruments for disease diagnosis is on a rise.
- Chemical equipment market is growing at a rapid rate due to the continuous requirement of these instruments in pharmaceutical and biotechnology industries.
- Besides, the increase in number of biotechnology firms worldwide, advances in life science research and technology innovations with human genome mapping, and emergence of proteomics have enabled industry growth; as such high-end research projects require quality instruments with high throughput capacity. All these factors are driving the life science and chemical instrumentation market.
- The global life science and chemical instrumentation market was estimated to be \$30.2 billion in the year 2011 and is expected to grow at a CAGR of 8.4% from 2011 to 2016 to reach \$45.2 billion.



**CONNECTION BETWEEN CHROMATOGRAPHY AND MS****Chromatography**

It is the collective term for a set of laboratory techniques for the separation of mixtures and for the detection of small amounts of materials present in those mixtures.

**Principle**

- The mixture is dissolved in a fluid called the *mobile phase*, which carries it through a structure holding another material called the *stationary phase*.
- The various constituents of the mixture travel at different speeds, causing them to separate.
- The separation is based on differential partitioning between the mobile and stationary phases. Slight differences in a compound's partition coefficient result in differential retention on the stationary phase and thus changing the separation.

**Mass spectrometry**

- It is an analytical technique that measures the mass-to-charge ratio of charged particles.
- It is used
  - ✓ for determining masses of particles,
  - ✓ for determining the elemental composition of a sample or molecule, and
  - ✓ for determining the chemical structures of molecules, such as peptides and other chemical compounds.
- It works by ionizing chemical compounds to generate charged molecules or molecule fragments and measuring their mass-to-charge ratios.

**Gas chromatography-mass spectrometry (GC-MS)**

It is a method that combines the features of gas-liquid chromatography and mass spectrometry to identify different substances, even present in small amounts, within a test sample.

**Applications**

- These include drug detection, fire investigation, environmental analysis, explosives investigation, and identification of unknown samples.
- GC-MS can also be used in airport security to detect substances in luggage or on human beings.
- It can identify trace elements in materials that were previously thought to have disintegrated beyond identification.
- GC-MS has been widely heralded as a "gold standard" for forensic substance identification because it is used to perform a *specific test*. A specific test positively identifies the actual presence of a particular substance in a given sample.

**Liquid chromatography-mass spectrometry (LC-MS, or alternatively HPLC-MS)**

It is a chemistry technique that combines the physical separation capabilities of liquid chromatography (or HPLC) with the mass analysis capabilities of mass spectrometry.

It has very high sensitivity and selectivity.

**Applications**

- Generally its application is oriented towards the general detection and potential identification of chemicals in the presence of other chemicals (in a complex mixture)
- Preparative LC-MS system can be used for fast and mass directed purification of natural-products extracts and new molecular entities important to food, pharmaceutical, agrochemical and other industries.

**Limitations**

- The limitations of LC-MS in urine analysis drug screening is that it often fails to distinguish between specific metabolites, in particular with hydrocodone and its metabolites.



- LC-MS urine analysis testing is used to detect specific categories of drugs. However, gas chromatography (GC-MS) should be used when detection of a specific drug and its metabolites is required.

### KEY POINTS

- The empirical formula of an organic compound can be found by analysis of its combustion products.
- The molecular formula of a compound can be found from the empirical formula once the relative molecular mass is unknown.
- The structural formula shows the precise arrangement of atoms. It can be found from a knowledge of some of the properties of the compound or by using instrumental methods, particularly mass spectrometry, infrared (IR) spectroscopy and nuclear magnetic resonance (NMR).
- The instrument that is used to measure the amount of electromagnetic radiation absorbed by an organic molecule is called Spectrophotometer or Spectrometer.
- Absorption of infrared radiation causes covalent bonds within the molecule to be promoted from one vibrational energy level to a higher vibrational energy level.
- Stronger bonds require greater energy to vibrate. Therefore such bonds absorb infrared radiation of shorter wavelengths.
- Different functional groups absorb infrared radiation at different wavelengths and their presence or absence in a molecule can be determined by examination of an IR spectrum.
- No two compounds have exactly identical infrared spectra.
- Absorption of ultraviolet visible radiation causes electrons within molecules to be promoted from one energy level to a higher electronic energy level.
- If an organic compound does not absorb UV-Vis radiation it means that the compound does not contain conjugated double bonds.
- If an organic compound absorbs UV-Vis radiation it means that the compound contains a carbonyl group or conjugated double bonds. For example, conjugated dienes, carbonyl compounds and aromatic compounds all absorb in the UV-Vis region.
- Absorption of radio waves in the presence of a magnetic field causes nuclei within molecules to be promoted from one spin energy level to a higher spin energy level.
- The number of signals in the NMR spectrum corresponds to the number of different types of protons in the molecules.
- The position (chemical shift) of each signal gives information about the structural environment of the protons.
- The relative areas (Integration) under the signals give the ratio of the numbers of each type of protons in the molecule. If the molecular formula is known, the actual number of each type of protons can be determined.
- The splitting pattern of each signal gives us the number of protons on neighboring carbons. The number of peaks into which a signal is split is one more than the total number of protons on directly adjacent carbons.
- Emission spectroscopy is concerned with the characteristic radiation produced when atoms are excited. They emit radiations in the form of discrete wavelengths of light, called spectral lines while returning to the lower energy states.
- Atomic absorption spectroscopy involves the study of the absorption of radiant energy, usually visible to neutral atoms in the gaseous states. If light of the resonance wavelength passes through a flame containing the atoms, then part of the light will be absorbed, and the extent of absorption will be proportional to the number of ground state atoms present in the flame.
- Mass spectroscopy involves organic molecules being bombarded by a very high-energy electron beam.
- The peak of highest intensity in a mass spectrum is referred to as the base peak.
- Fragmentation processes can produce numerous fragments from which the structures of organic molecules can be deduced.
- When one electron is removed from a molecule, a molecular ion is produced. The  $m/e$  value of the molecular ion peak is the molecular weight of the compound being investigated. The molecular weights obtained by mass spectroscopy are extremely accurate.



## EXERCISE

**1. Select the right answer from the choices given with each question.**

Which of the following techniques does not involve electromagnetic radiations?

- (a) Infrared spectroscopy (b) NMR spectroscopy  
(c) Mass spectroscopy (d) All of these involve electromagnetic radiations

Which region of the electromagnetic spectrum is involved in the electronic excitations?

- (a) Ultraviolet (b) Visible  
(c) Both of these (d) None of these

Which of the following techniques is different from the others as regards the basic principle?

- (a) Ultraviolet spectroscopy (b) Visible spectroscopy  
(c) Electronic spectroscopy (d) None of these

Which of the following is used as a source of visible radiations?

- (a) Tungsten filament lamp (b) Hydrogen discharge lamp  
(c) Deuterium discharge lamp (d) All of these

What is the wavelength range of the ordinary infrared region?

- (a) 0.8-2.5  $\mu\text{m}$  (b) 2.5-16  $\mu\text{m}$   
(c) 16-1000  $\mu\text{m}$  (d) 400-800 nm

ii) The position of an infrared absorption band is commonly expressed by:

- (a) Wavelength (b) Wave number  
(c) Both of these (d) None of these

iii) Which of the following is not used as a source of infrared radiations?

- (a) Nernst filament (b) Tungsten filament  
(c) Globar (d) None of these

iv) Which region of the electromagnetic spectrum is involved in mass spectrometry?

- (a) Visible (b) Microwave  
(c) Radiowave (d) None of these

v) Mass spectroscopy is an analytical technique which involves:

- (a) Production of gaseous ions from the sample  
(b) Separation of the gaseous ions  
(c) Measurement of the relative abundance of the gaseous ions  
(d) All of these

vi) Mass spectrometry can be used to determine:

- (a) Molecular weight (b) Molecular formula  
(c) Molecular structure (d) All of these

vii) Which of the following species is detected in the mass spectrometer?

- (a) Positively charged species (b) Radicals  
(c) Neutral molecules (d) All of these

viii) Which of the following species is produced in the ionization chamber of a mass spectrometer?

- (a) Positively charged species (b) Radicals  
(c) Neutral molecules (d) All of these

ix) Which kind of information about a positively charged species obtained from a mass spectrum?

- (a) Molecular weight (b) Relative abundance  
(c) Both of these (d) None of these

x) What kind of sample can be studied in a mass spectrometer?

- (a) A gas (b) A liquid  
(c) A solid (d) All of these

xi) Near ultraviolet region of the electromagnetic spectrum generally lies between:

- (a) 10-200 nm (b) 200-400 nm  
(c) 400-750 nm (d) 300-500 nm

xii) For ultraviolet or vacuum ultraviolet region generally lies between.



CH = 2e-4 molar Chemistry

- (a) 10-200 nm  
(c) 400-750 nm

- (b) 200-400 nm  
(d) 300-500 nm

(xvii) Far infrared region of the electromagnetic radiation generally lies between:

- (a) 50-200  $\mu\text{m}$   
(c) 50-1000  $\mu\text{m}$

- (b) 100-400  $\mu\text{m}$   
(d) 1-20  $\mu\text{m}$

## ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (c) Mass spectroscopy

In this a beam of electrons is used

(ii) Ans: (c) Both of these

Both ultraviolet and UV rays cause electronic excitation

(iii) Ans: (d) None of these

All techniques are based upon the electronic excitations

(iv) Ans: (a) Tungsten filament lamp

Tungsten filament lamp produces visible light

(v) Ans: (b) 2.5-16  $\mu\text{m}$

It is the ordinary infrared region

(vi) Ans: (b) Wave number

It is on X-axis

(vii) Ans: (b) Tungsten filament

It is used for visible light

(viii) Ans: (d) None of these

Radiations are not used in Mass Spectrometry

(ix) Ans: (d) All of these

All these are involved in Mass spectrometry

(x) Ans: (d) All of these

All these can be determined

(xi) Ans: (a) Positively charged species

Since, ions with positive charge are separated on the basis of their m/e value

(xii) Ans: (a) Positively charged species

Positively charged species are produced by bombardment of electrons.

(xiii) Ans: (c) Both of these

Both are obtained from Mass Spectrometry

(xiv) Ans: (d) All of these

All can be studied. However, liquid and solid must be vaporized.

(xv) Ans: (b) 200-400 nm

This region is near the visible region. So it is called near UV region.

(xvi) Ans: (a) 10-200 nm

This region is far from the visible region. So it is called far UV region.

(xvii) Ans: (c) 50-1000  $\mu\text{m}$

It is far infrared

## Q2: Give brief answers for the following questions.

(i) What is spectroscopy? Underline its principle.

**Spectroscopy:** Spectroscopy involved using instruments to examine the radiation emitted or absorbed by chemicals giving information about their molecular structure.

**Principle:** When electromagnetic radiation, such as light or infrared, shines on a chemical the chemical interacts with the radiation in some way. The way a particular chemical interacts with radiation can tell about its molecules and structure.

(ii) What is meant by wavelength and frequency?

### Wavelength

It is the distance between two adjacent crests or troughs in a beam of radiation.

It is denoted by  $\lambda$ .

Its units are picometer, nanometer or angstrom etc.

$$1 \text{ \AA} = 10^{-10} \text{ m}, 1 \text{ nm} = 10^{-9} \text{ m}, 1 \text{ pm} = 10^{-12} \text{ m}$$

### Frequency

It is the number of waves, which passes through a given point in one second.

It is denoted by  $\nu$ . Its units are cycles  $\text{s}^{-1}$  or  $\text{s}^{-1}$  or Hertz (Hz).

$$1 \text{ Hz} = 1 \text{ cycles s}^{-1}$$



(i) What is spectrometer? Briefly discuss its working.

**Spectrometer:** The instrument used to measure the amount of radiations absorbed by a substance is called spectrometer.

**Working:** In a spectrometer, the electromagnetic radiations are passed through a sample. The radiations absorbed by a sample are recorded in the form of a graph. This graph is called spectrum. The spectrum can be used to find information about structure of a substance.

(ii) How will you distinguish between

(i) 1,3 -Pentadiene and 1,4 -Penta-diene

1,3-Pentadiene is a conjugated system ( $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$ ) while 1,4-pentadiene is not a conjugated system ( $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$ ). Therefore, 1,3-pentadiene will absorb at higher wavelength and have higher  $\lambda_{\text{max}}$  than that of 1,4-pentadiene.

(ii) Benzene and anthracene by UV -spectroscopy?

Anthracene molecule has three benzene rings. So it has more conjugation than benzene. Therefore anthracene will absorb at higher wavelength and have higher  $\lambda_{\text{max}}$  than that of benzene.

(iii) Two isomeric dienes (X) and (Y), having the molecular formula  $\text{C}_5\text{H}_8$ , absorb at  $\lambda_{\text{max}}$  223nm and  $\lambda_{\text{max}}$  178nm respectively. Write the structures of the two isomers.

These are 1,3-Pentadiene and 1,4-Pentadiene.

1,3-Pentadiene is a conjugated system ( $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$ ) while 1,4-pentadiene is not a conjugated system ( $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$ ). Therefore, 1,3-pentadiene will absorb at higher wavelength ( $\lambda_{\text{max}}=223\text{nm}$ ) than that of 1,4-pentadiene ( $\lambda_{\text{max}}=178\text{nm}$ ).

(iv) Give significant application of Atomic Absorption Spectroscopy (AAS).

(1) This method is well-suited to the analysis of a substance at low concentration.

(2) This method is highly specific, hence analysis of a metal from a complex mixture is possible.

(3) The technique is firmly established in analytical chemistry, ceramics, mineralogy, biochemistry, metallurgy, water supplies and soil analysis.

(v) How will you distinguish between 2-Pentanone and 3-Pentanone by using mass spectra?

2-Pentanone: Its major peak (base peak) in mass spectrum is  $m/e=43$ .

3-Pentanone: Its major peak (base peak) in mass spectrum is  $m/e=57$ .

### Q3: Give detailed answers for the following questions.

(i) What is combustion analysis? Describe its different steps.

Page 496

(ii) An organic compound consists of carbon, hydrogen and oxygen. It was subjected to combustion analysis. 0.5439g of the compound gave 1.039g of  $\text{CO}_2$  and 0.6369g of  $\text{H}_2\text{O}$ . Determine the empirical formula of the compounds.

**Solution:**

Mass of organic compound = 0.5439g

Mass of  $\text{CO}_2$  = 1.039g

Mass of  $\text{H}_2\text{O}$  = 0.6369g

Thus Percentage of C

$$\frac{1.039 \times \frac{12}{44}}{0.5439} \times 100 = 52.11\%$$

Percentage of H

$$\frac{0.6369 \times \frac{2 \times 1}{18}}{0.5439} \times 100 = 13.11\%$$

Percentage of O

$$= 100 - (52.11 + 13.11) = 34.78\%$$



$$\begin{aligned}\text{Percentage of H} &= \frac{0.6369}{0.5439} \times \frac{2.016}{18} \times 100 = 13.12\% \\ \text{Percentage of O} &= 100 - (52.11 + 13.11) = 34.78\%\end{aligned}$$

ELEMENT	%	No. of gram atoms	Atomic Ratio	Empirical Formula
C	52.10	$\frac{52.10}{12} = 4.34$	$\frac{4.34}{2.17} = 2$	$C_2H_6O$
H	13.12	$\frac{13.12}{1.008} = 13.02$	$\frac{13.02}{2.17} = 6$	
O	34.78	$\frac{34.78}{16} = 2.17$	$\frac{2.17}{2.17} = 1$	

Thus the empirical formula for the organic compound is  $C_2H_6O$

- (iii) The combustion analysis shows that organic compounds contain 65.44% carbon, 5.50% hydrogen and 29.06% of oxygen. What is empirical formula? If the molecular mass of this compound is  $110.15 \text{ g mole}^{-1}$  then calculate molecular formula of given organic compound. (Ans:  $C_3H_8O$ ,  $C_6H_{16}O_2$ )

Solution:

ELEMENT	%	No. of gram atoms	Atomic Ratio	Empirical Formula
C	65.44	$\frac{65.44}{12} = 5.45$	$\frac{5.45}{1.82} = 3$	$C_3H_8O$
H	5.50	$\frac{5.50}{1.008} = 5.45$	$\frac{5.45}{1.82} = 3$	
O	29.06	$\frac{29.06}{16} = 1.82$	$\frac{1.82}{1.82} = 1$	

Thus the empirical formula is  $C_3H_8O$ .

To determine the molecular formula, first calculate the empirical formula mass.

$$\text{Empirical formula mass of } C_3H_8O = 12 \times 3 + 1.008 \times 8 + 16 \times 1 = 55.05 \text{ g mol}^{-1}$$

$$\text{Molecular (or molar) mass of the compound} = 110.15 \text{ g mol}^{-1}$$

$$n = \frac{\text{molecular mass of compound}}{\text{empirical formula mass of compound}} = \frac{110.15}{55.05} = 2$$

$$\begin{aligned}\text{Thus Molecular formula} &= n (\text{empirical formula}) \\ &= 2 (C_3H_8O) \\ &= C_6H_{16}O_2\end{aligned}$$

- (iv) What is meant by the term chemical shift of a particular proton in NMR spectroscopy? Also draw the splitting pattern of protons in NMR spectrum of ethyl alcohol. Page 505
- (v) Discuss the general principle and instrumentation of Atomic Emission Spectroscopy. What is the basic principle of Atomic Absorption Spectroscopy? Describe the instrumentation used. Page 512
- What is the basic principle of Mass Spectrometer? How does it work? Page 513



TEST YOUR SKILLS

OBJECTIVE

Marks: 85

Time: 20 Minutes

Marks: 17

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks

Q1. Circle the correct option i.e. A/B/C/D. Each part carries one mark.

- (i) A ..... is an instrument which allows radiation to interact with sample of chemical and analyze the changes.  
(A) combustion chamber (B) spectroscope (C) Mass spectrum (D) HPLC - MS
- (ii) Infrared radiation makes the bonds of molecule to .....  
(A) excite (B) rotate (C) vibrate (D) None
- (iii) ..... radiation excites the electrons from lower energy level to highest level.  
(A) ultraviolet (B) Visible (C) Microwaves (D) both a & b
- (iv) ..... involves radio waves  
(A) Nuclear magnetic resonance (B) Electron spin resonance  
(C) Mass Spectrometry (D) both a & b
- (v) IR absorption is used to identify bonds and ..... in an organic compound  
(A) no. of carbon atoms (B) functional groups (C) rotation (D) none of these
- (vi) Which of following techniques does not involve electromagnetic radiation?  
(A) NMR Spectroscopy (B) Infrared Spectroscopy  
(C) Mass Spectroscopy (D) All of these
- (vii) Which of the following is used as source of visible radiations?  
(A) Tungsten filament lamp (B) Deuterium discharge lamp  
(C) Hydrogen discharge lamp (D) none
- (viii) In IR spectrum of propanone, strong peak is at about  $1720\text{ cm}^{-1}$  which refers to ..... bond  
(A) C - C bond (B) C - H bond (C) C = O bond (D) both a & c
- (ix) In IR spectrum of propanone which absorption at ..... refers to C - H bond  
(A)  $1600\text{ cm}^{-1}$  (B)  $2500\text{ cm}^{-1}$  (C)  $3000\text{ cm}^{-1}$  (D)  $1900\text{ cm}^{-1}$
- (x) Useful and interesting region of IR spectrum is the region above .....  
(A)  $1500\text{ cm}^{-1}$  (B)  $2000\text{ cm}^{-1}$  (C)  $3000\text{ cm}^{-1}$  (D)  $3400\text{ cm}^{-1}$
- (xi) A solution of titanium (III) chloride appears violet, it absorbs which region of spectrum?  
(A) green (B) yellow (C) green - yellow (D) Red
- (xii) In mass spectrometry, ions with ..... mass / charge ratio will be deflected smaller  
(A) smaller (B) greater (C) particular (D) None
- (xiii) The position of ultraviolet - visible absorption band is commonly expressed by  
(A) Wave length (B) Wave Number (C) both (D) None
- (xiv) Why do transition metal compounds show colour  
(A) due to incomplete d- orbital's (B) due to metallic nature  
(C) because of excitation of molecule (D) all of these
- (xv) HCl molecule absorbs IR radiation of frequency .....  
(A)  $7.21 \times 10^{13}\text{ Hz}$  (B)  $6.2 \times 10^{11}\text{ Hz}$  (C)  $5.5 \times 10^{12}\text{ Hz}$  (D)  $1.6 \times 10^{13}\text{ Hz}$
- (xvi) ..... is chosen as NMR reference  
(A) ethyl benzene (B) ethanol (C)  $\text{H}_2\text{O}$  (D) tetramethylsilane
- (xvii) Which of the following species is detected in mass spectrometer?  
(A) Radicals (B) Positively charged species  
(C) Neutral molecules (D) All of these

(i) SUBJECTIVE

(ii) Time: 2:35 Hours

Total Marks Section B and C: 68

(iii) Section - B (Marks 42) ( $14 \times 3 = 42$ )

Q2. Attempt any FOURTEEN parts. The answer to each part should not exceed 5 to 6 lines.

- (i) (a) Differentiate between Qualitative & Quantitative analysis. (2)  
(b) Define Analytical chemistry. (1)
- (ii) (a) Define Spectroscopy. (1)  
(b) Describe different types of Spectroscopy. (2)
- (iii) Describe characteristic significance of IR Spectroscopy (3)
- (iv) How does IR spectroscopy explain type of bonds & functional group in case of propanone (3)
- (v) (a) Why transition metal compounds are coloured. (1)  
(b) What happens when radiation strikes a substance? (2)
- (vi) Describe why methylene blue is blue in colour? (3)
- (vii) Aqueous solution of Titanium (III) chloride is violet in color. Explain the phenomena behind this. (3)
- (viii) What is significance of NMR Spectroscopy?
- (ix) (a) What is NMR Reference? (1)  
(b) Why splitting of peaks occur in NMR spectrum. (2)
- (x) (a) How emission spectroscopy is applied in metallurgy? (1.5)  
(b) How lubricant oil can be analyzed by emission spectroscopy. (1.5)
- (xi) (a) Describe the basic principle of Atomic Absorption Spectroscopy. (2)



- (b) Which type of elements and samples are analyzed by AAS. (1)
- (xii) (a) Name main steps involved in mass Spectrometer. (1.5)
- (b) How sample is ionized in mass Spectrometer. (1.5)
- (xiii) How ion detector works in mass Spectrometer. (3)
- (xiv) Describe basic principle of chromatography. (3)
- (xv) (a) What is LC - MS? (1)
- (b) Describe applications of GCMS. (2)
- (xvi) How will you distinguish between. (3)
- (a) Pentanone and (b) Rentanone by using mass spectra. (3)
- (xvii) Differentiate between atomic absorption Spectroscopy and atomic commission Spectroscopy. (3)
- (xviii) (a) What is wavelength of IR & UV. (2)
- (b) Which colour of visible light clear methylene blue absorb? (1)
- (xix) (a) What is drawback of combustion analysis? (1)
- (b) Name modern methods of analysis. (2)

**Section - C**

**Note:** Attempt any TWO questions. All questions carry equal marks. ( $2 \times 13 = 26$ )

- (a) How molecular formula of organic compound is determined by combustion analysis? (5)

(b) An organic compound consist of C, H, O was subjected to combustion analysis 0.5438 g of compound g are 1.039 g of  $H_2O$ . determine empirical formula of compounds. (4)

(c) How different types of radiation interact with chemicals. (4)
- (a) Define IR Spectroscopy. How IR spectroscopy is applied to analyze different compounds. (5)

(b) Describe Spin - spin coupling in NMR Spectroscopy. (4)

(c) Explain advantages & Disadvantages of AES. (4)
- (a) Explain instrumentation & working of Mass Spectrometer. (4)

(b) Describe application of AAS. (5)

(c) How chromatography and MS can be helpful in analysis if combined together. (4)
- (a) Explain chemical shift of particular proton in NMR spectroscopy using example. (5)

(b) How analytical chemistry benefits in field of Forensic sciences. (4)

(c) Discuss application of Atomic emission spectroscopy. (4)



